



A TYPICAL RUBBER TREE.

FROM THEORY TO PRACTICE
IN
RUBBER FABRICATION.

VOLUME II.

By

JOHN HELEN

Late Rubber Expert to the Government of Travancore.

PRINTED AT
THE SANTA CRUZ PRESS, ALLEPPEY.
1944.

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Addenda

The additions listed below refer to new formulas etc., that have been composed since the printing of this Volume began. They should be consulted at the right place and used accordingly.

THE AUTHOR.

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94 7 Add the following mix:—

Alkali Reclaim (without lumps)	147 ^k	000
Zinc Oxide 	5	250
Kaolin 	12	750
Barium Sulphate ...	4	400
Calcium Carbonate 	1	800
Cycline Oil 	2	000
Stearic Acid 	0	550
Mineral Rubber 	10	000
Rosin 	10	000
Tackol 	6	600
Sulphur 	0	885
RN-2 Crystals 	0	220
	201 ^k	455

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The above mix should be dissolved in about 60 gallons of solvent. The solution is self-vulcanising. There is no need for making two distinct batches. The RN-2 Crystals can be dissolved in the solvent and added to the solution when ready to be used. To prevent the mix from sticking to the roller the Rosin can likewise be dissolved in the solvent and added, in the Stirring Mill, at the same time when the dry mix is being dissolved.

Remarks. It should be noted that there is no such product as a "*Solution from Reclaim*", for reclaim can never be dissolved in solvent. The so called "*Solution from Reclaim*" is a dough in which the molecules of the reclaimed rubber waste are in suspension, but not dissolved; and such kind of "*Solution*" could never be tacky but for the Rosin and the Tackol present in the mix.

99 7 Add:—

Self-vulcanising Cement from Reclaim 214%
on the weight of dry solution.

99 12 Add:—

With Solution from Reclaim.

(a) Muslin 5 oz. per sq. yd. in 4 coats,

(b) Sheeting 5 oz. " " " " 4 "

151 11 Add:—

In factory practice, with skilled labour, it is even possible to strip the dipped goods from the formers *before* the vulcanisation takes place.

Preface.

I have pleasure in introducing to the Rubber Manufacturing Public, and to all those interested in the Rubber Industry, the Second Volume of "*From Theory to Practice in Rubber Fabrication.*"

If the First Volume was the outcome of numerous enquiries, that I have received from time to time, relating to rubber manufacture, the Second Volume is the result of a desire to give still further information regarding the manufacture of rubber goods, and the various developments which are continuously taking place in the Rubber Industry. The field is certainly too large to be covered within the pages of the two volumes I have written dealing with the theory and practice in rubber fabrication, but it has been my endeavour to give up-to-date information on all subjects of interest, and also up-to-date formulas for the manufacture of various rubber goods which are in general use all over the world.

All the copies of the first volume of "*From Theory to Practice in Rubber Fabrication*", printed in 1942, were exhausted within a few months of publication, and the eagerness with which they were welcomed by the Rubber Manufacturer, and others, is clear proof of the gap which they have helped to fill in the technical world, and also the great need of such kind of books.

The publication of the first volume was the occasion for various appreciative comments, too

numerous to reproduce in this preface. A few of these comments will suffice.

"From what I can see of your rubber book", wrote Mr. T. J. Crane of the Monsanto Chemicals Ltd., Ruabon, "it should rank as one of the few really practical text books existing on Rubber Technology."

Mr. E. F. M. Norman, Planter Trichur, writes:

"I thank you for your book and congratulate you on bringing out a most useful book on rubber manufacture. I am particularly pleased that you have devoted some space to Latex Work in which branch I am most interested."

The Editor of the "South Indian Bulletin" of the European Association wrote:—

"This is a small volume packed with information valuable to the manufacturer of rubber goods and to those who aspire to set up rubber working factories. For the former it provides an opportunity to bring his technical knowledge up-to-date, to the latter it shows clearly that rubber factories are not concerns to be established and run by amateurs, but that on the contrary their success depends to a great extent on the technical knowledge, experience, and skill of the person in charge. We wish the book all success. It should assist the trained manufacturer to develop his business, and restrain the untrained and inexperienced from venturing into industrial fields best left to be exploited by specialists".

'B.B.D' in the "Hindu" concludes his comments by stating:

"The book is copiously illustrated and has a strong practical bias, which constitute its chief merits for recommendation as a valuable guide to the manufacturer of rubber goods in India".

Since the publication of the first volume, Synthetic Rubber has taken a greater part in the Rubber Industry and it is generally feared that it might totally replace the natural product. This raises a great issue and is

fully discussed in a chapter specially devoted to this subject.

With regard to the chemicals, etc. recommended in Volume II, for incorporation in rubber mixes, wherever mention is made of Vulcafor SPX, DDC, SDC, ZIX, DDCN, P, DHC, ZDC, TMT, TET, MS, Vulcatac CH, Vulcatac III, Rubber Mastication Paste ICI, Neoprene, Neozone D, Dispersol LN and Alloprene Mixtures, all these products are the trade marks belonging to the *Imperial Chemical Industries Ltd., London*. All other chemical denominations mentioned in this book, except otherwise stated, are the trade marks of the *Monsanto Chemicals Ltd., Ruabon*.

I would warn all those who may be interested in the industrial application of synthetic rubbers, and the latex technology, that the field is much encumbered with patents, many admittedly of doubtful validity. The matter is exceedingly complicated, and it has consequently not been possible to deal with patent questions in this volume. I am furthermore unable to guarantee that any of the processes, or formulas given, or commented on, in the following pages, are free from such restrictions. Advice should therefore be sought on the patent position before manufacture is commenced. It should also be remembered that, in certain patents, while the provisional specification seeks to protect application of the process to latex of any type, or to synthetic rubbers, the accepted specification only confers protection on its application to a single proprietary brand. Thus, unless the printed copy of the specification is read with care, a false impression of the scope of the patent may easily arise.

THE AUTHOR.

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FROM THEORY TO PRACTICE IN RUBBER FABRICATION.

CHAPTER I.

Generalities.

EXACTLY 102 years ago, a Yankee of Connecticut —Charles Goodyear—made his name immortal.

In his early days, he planned to study for the Holy Ministry, but changed his mind and some time later started his own hardware shop in Philadelphia, where he shortly afterwards went bankrupt. He was the son of an inventor, who made metal buttons for the American Army uniforms during the war of 1812. The son followed the footsteps of the father, and turned his mind to inventions. As already mentioned in Volume I he had seen an article made of tacky rubber, and it occurred to him that tacky rubber, if properly worked, would be useful to mankind. He at once started experimenting, spending time and money, at this work. He borrowed huge sums of dollars to carry on his work of research and went so far that he even appropriated his wife's last silk petticoat to produce a rubberised hat! Time and again he was declared bankrupt and was thrown into the debtors' prison where he finally died an insolvent!

At about the same time that Charles Goodyear of New England was trying to make tacky rubber non-sticky, and perhaps elastic, another inventor—Thomas Hancock—of Old England tackled the rubber problem in another way, by devising the first rubber masticator and the first calender to reduce the masticated rubber into sheets, and in this way became the Father of the Rubber Industry, whereas Charles Goodyear was rightly styled the Father of Vulcanisation!

Since those early days marvels have been produced in the Rubber Industry. The Goodyear epoch was one of inventions, whereas we are now living in an epoch of specialization. In this gigantic world struggle some men are specializing in improving machines; others are modifying the aeroplanes of yesterday and are producing bigger and faster machines capable of transporting more and more load; still others are creating rockets loaded with heavy bombs which fly through the air, to determined areas, where they cause havoc; shipbuilders are supplying Navy Units in a day's time for which, in pre-war time, months, if not years, were needed! In all these innovations, there seems to be such an interlocking of wheels within wheels, that one loses the proper perspective; or say the proper sense of values.

There is more and more specialization not only in the mechanical world, but also in the field of chemistry, where men are trying to compose more synthetics to replace the lost supply of raw rubber, despite the fact that almost every day brings the discovery of a new plant in the botanical world, capable of yielding the precious and indispensable latex!

In the Rubber Industry also, the wonderful accelerators are following the path of Progress, and

the rubber technologist realises the important role these have to play in the field of vulcanisation. A few years ago, it was considered sufficient just to have an article vulcanised, and, provided it did not deteriorate in a given time, it was declared good. This is no more the case now-a-days. Because of the appearance of all these accelerators, the fabrication of rubber is no longer a combination of rubber with sulphur and fillers, but is now based solely on chemical actions and reactions, so that one wonders when and where there will be an end to the sensational improvements caused by all these chemical discoveries.

The number of accelerators increases every day, and new types with still better and astonishing properties are being discovered either modifying or supplementing those still being used in the factory, thus satisfying the increasing daily demands of the manufacturer who is now convinced that without these accelerators he can get nowhere.

The researches of the rubber chemists are thus being continually stimulated, and combinations of accelerators, even of different chemical properties, have been found with the result that rubber articles can now be vulcanised in the course of a few seconds! Such vulcanisation can, however, only be obtained at temperatures not lower than 200° C.—a temperature which cannot be attained in most of the factories with their existing boilers and vulcanisers! An electrically heated wooden tank, protected by asbestos and lined with copper is essential for this kind of vulcanisation. But it should be remembered that “*accelerator*” is not always synonymous with “*speed*”. In fact one of the major duties of the accelerator is to promote an improvement in the quality of the rubber. Even

with Ultra-accelerators, which we have already discussed in Volume I, satisfactory results are not always obtainable with short cures at high temperatures, the real properties of these Ultra-accelerators being brought out only when the vulcanisation is done over a relatively longer period of time and at a much reduced temperature, so much so that present Ultra-accelerators give their best properties when used at temperatures ranging from 100 to 125° C., it being understood that, with higher temperatures, they give a sharp peak of vulcanisation, and from that point onwards usually a rapid depolymerization or a reversion of the stress-strain-curve takes place, so that we may be sure that we are starting the reclaim of the outside of a tube before the inside becomes vulcanised!

If that is so, and taking into consideration that some of the Ultra Accelerators are capable, in a given time, of vulcanising the rubber at room temperature, then why not reduce the temperature of the vulcanisation from 125 to 100° C., and why not cure the rubber mix so compounded in boiling water? It is self-evident that precautions are to be taken to have the product thoroughly vulcanised in such a way. (It is intended to revert to this matter in subsequent pages.) This is another reason why, if vulcanisation in boiling water has been adopted, olden types of vulcanisers can be removed from our existing rubber factories, and replaced by tanks of different sizes and capacities: long ones capable of receiving the mandrels covered with rubber hoses, others big enough to have immersed in them drums with rubber sheets, and still others in which to plunge the moulds. And when the use of latex, instead of pale crepe or smoked sheets, will be more generally adopted in rubber factories, the heavy duty mills and the mammoth

calenders can be discarded with the result that the equipment of the rubber factory can be simplified from top to bottom.

Does this mean that the rubber manufacturing process will then be less difficult and the raw rubber may be more homogeneous, so that we may expect to turn out a standardized product from a standard raw material? We do not think so, because raw rubber is one of the most variable raw materials known to man. The same kind of rubber trees growing on opposite sides of a hill yield different kinds and qualities of latex. It seems quite clear that with the use of all the accelerators which had existed previously and the new ones which are now produced, the properties and uses of which are explained in subsequent pages, we can still not be definitely sure of what rubber fabrication has in store for us.

Before proceeding, however, it is desirable to explain some of the technical terms employed in the Rubber Industry. These were briefly dealt with in Volume I, page 147, but it would probably be useful to reproduce in extenso* details regarding them, as published in the "British Standard Methods of Testing Vulcanised Rubber" - June 1940.

Tensile Strength is the load, per unit area of the original cross-section, required to stretch the rubber to breaking point, the conditions being such that the stress is substantially uniform over the cross-section.

Elongation at Break is the increase in length expressed as a percentage of the original length of a piece of rubber of uniform cross-section, when stretched to breaking point.

*With the kind courtesy of P. Good Esq., C. B. E., Director, British Standards Institutions, Westminster, London S. W. 1.

Elongation at Constant Load (L) is the increase in length, expressed as a percentage of the original length, of a piece of rubber of uniform cross-section, when subjected to a load L per unit area of the original cross-section.

Modulus at a given elongation (E per cent) is the load, per unit area of the original cross-section from the unstrained condition to an elongation of E per cent.

Permanent Set is the residual deformation of a specimen of rubber after subjection to stress. In the methods of test, permanent set is measured as the residual increase in length, expressed as a percentage of the original length, of a piece of rubber of uniform cross-section, after being stretched (a) to a given percentage elongation, or (b) under a given load (per unit area of original cross-section), for a given time and then allowed to recover for a given time, the temperature being substantially constant during the test.

Hardness is expressed as **Hardness Number**. This is the difference between the depths of penetration (expressed in 100ths of a mm.) of a rigid ball $3/32$ inch diameter pressed perpendicularly on to the surface of a piece of the rubber of stated thickness by loads of 30 g. and 565 g., the loads being allowed to act for 5 and 30 seconds respectively.

Electrical Breakdown Strength is the electric stress required to produce a disruption discharge through the body of the material. It varies with the thickness tested, and other factors.

Electrical Surface Resistivity is the electrical resistance between opposite edges of a square surface of the material.

Electrical Volume Resistivity is the electrical resistance between opposite faces of a unit cube of the material. It varies with the duration of application of the electric stress.

The Permittivity of a material is the ratio of the capacity of a condenser having the material as dielectric to the capacity of a similar condenser having air, or more precisely a vacuum, as dielectric, the measurements being made with alternating current. It usually varies in a small degree with the frequency of the applied voltage.

Power Factor is the ratio of the power loss in the material when used as the dielectric of a condenser to the total power transmitted through the condenser (product of the applied voltage and the resultant current). It usually varies with the frequency of the applied voltage.

Swelling is measured as the volume of liquid absorbed per 100 volumes of the original rubber composition, when a test piece of given dimensions is (a) immersed in, or (b) exposed to the vapour of, a liquid for a given time and at a given temperature. The amounts absorbed from vapour (even saturated vapour) and directly from the corresponding liquid are not necessarily the same.

Water Absorption is measured as the volume of water absorbed when a rubber test piece of given dimensions is immersed (a) in water, or (b) in a stated aqueous solution, or (c) exposed to aqueous vapour of given relative humidity, for a given time and at a given temperature. "Equilibrium" water absorption, expressed as volume absorbed per 100 volumes of original rubber composition, is independent of the dimensions

of the test piece, and is conveniently determined on finely-divided material, because attainment of "equilibrium" absorption is otherwise too slow. Exposure to vapour of a given relative humidity gives substantially the same "equilibrium" absorption as immersion in a solution which would be in equilibrium with the given vapour, apart from effects due to extraction of water-soluble constituents in the latter case.

The result of short period tests or massive test pieces which give indication of the initial rate of absorption only, do not necessarily bear any relationship to those of "equilibrium" absorption tests.

Permeability to a specified gas, as applied to rubberised fabrics, is measured as the volume of the gas (corrected to 760 mm. and 20° C) passing through unit area of the fabric in unit time at a given temperature (normally 20° C.) when the partial pressure difference of the gas on the two sides of the fabric is a given amount. Permeability is usually expressed in litres per square meter per 24 hours.

Accelerated Ageing tests are designed to estimate the relative resistance of rubbers to deterioration with the passage of time. The tests are essentially comparative, and close correlation with the natural life of the rubber is not implied.

Test specimens are subjected to controlled deteriorating influences for definite periods, after which their properties are measured.

Deterioration should be measured by the changes in the property or properties which are of practical importance and which can be measured accurately.

Cross-breaking strength of Ebonite is defined as the load required to fracture, by bending, a bar-shaped

specimen of rectangular cross-section supported horizontally at two points, a given distance apart, the load being applied midway between them. The method given is a proof test in which the specimen must not fail under a given load.

Impact Strength or Toughness of Ebonite (the inverse of brittleness) is defined as the energy of the blow required to fracture or damage a bar-shaped test piece of given dimensions held as a cantilever and struck near the free end. It is sometimes expressed as energy per unit area of the cross-section of the test piece where the fracture occurs, but it varies with the shape of the cross-section. The method given is a proof test in which the specimen must not fail under a specified blow.

Plastic Yield of Ebonite is measured as the total deformation of a bar-shaped test piece of given dimensions, stressed under given conditions, viz., cantilever loading at a given temperature for a given time.

Compressive Strength of Ebonite. This is defined for practical purposes as the maximum compressive load that a test piece of given dimensions will withstand without crushing or showing more than a specified deformation.

CHAPTER II.

Accelerators.

A brief discussion of the Ureka group of accelerators should first of all command our attention. We know that Monsanto have already made numerous attempts in the past to use a combination of Accelerators to obtain the good qualities imparted to rubber by each accelerator and eliminate the bad features. Using combinations of different types of Accelerators, the Chemist has usually found that the increase in acceleration, when combinations were used, was not additive, but of some higher order. In fact combinations have been found which vulcanise so rapidly at low temperatures that they cannot be handled in the factory without the addition of retarders or specially designed machinery.

Realising the advantage of using mixtures as accelerators, Monsanto in 1928 produced the accelerator "*Ureka*". It consists of a mixture of "D. P. G." plus 2-4 Dinitro Phenyl Thio Benzothiazole, and it was the first time that an accelerator which was a mixture of two unlike organic materials made its appearance. Through the use of Ureka the Chemist was able to obtain high tensile and high modulus stocks and at the same time could handle these stocks safely.

Ureka found thus almost instant favour among the Rubber Chemists, who adopted it for tyres, tubes, sheetings, shoe stocks and the like.

But as the amount of acceleration necessary for satisfactory vulcanisation is higher in dry heat oven cures, it was deemed advisable to find an accelerator which was slightly slower in the rate of cure. This was obtained by replacing a portion of the "Diphenyl Guanidine" in Ureka with Guantal, which is Diphenyl Guanidine Phthalate, and the resultant material was named "**Ureka Blend B**", so much so that "Ureka Blend B" has replaced Ureka, in stocks in which more delayed action is required, and those plants having difficulty in handling Ureka, due to the high amount of accelerator necessary for proper vulcanisation, find Ureka Blend B most desirable.

Ureka Blend B, is thus a blend similar to Ureka with a portion of the D. P. G. replaced by Guantal. Its specifications and properties are:—

In appearance a yellow to brownish powder,
 A fineness of at least 99.5%, through a 200 mesh
 having no coarse particles,
 Has less than 2% moisture (which is the water
 present as water of crystallization in Guantal),
 Has less than 0.5% of ash,
 and a melting point of not less than 130° C.
 Its specific gravity is 1.33.

In view of the similarity of "Ureka Blend B" to Ureka, the former can be substituted for Ureka wherever it is desirable to do so. In view of its more pronounced delayed action and the resultant greater ease of handling, "Ureka Blend B" is apparently adopted for the dry vulcanisation of footwear. The increased amount of acceleration necessary for this type of cure makes the handling of Ureka stocks difficult due to the tendency to scorch.

Furthermore, "Ureka Blend B" possesses the property in dry heat vulcanisation of producing dry

hard surface stocks without the slightest indication of tack. This feature of the accelerator has eliminated the necessity in many instances of the use of varnishes, and has resulted in the saving of large amounts of money to the Rubber Footwear Industry.

Now, as the ratio of activator to 2-4 Dinitro Phenyl Thio Benzothiazole was fixed, the compounder using Ureka and "Ureka Blend B" was limited to one speed of acceleration at all times. This is not always desired, as it is sometimes better to have different ratios of acceleration depending on the article to be vulcanised. Realising this, Monsanto has produced the "*Ureka C*", which is a pure material and usually not active enough when used by itself, so that it is best to have an activator to obtain the best results. By the proper choice of an activator and the amount used, with Ureka C, the compounder can control at will the speed of acceleration, the modulus and tensile. In other words, by the use of "Ureka C" plus an activator, the compounder can obtain slow or fast curing stocks, high tensile high modulus stocks or low tensile low modulus stocks, depending entirely on the amount of the activator used.

Ureka C is an Acyl-Thiazole powder in which the acidic hydrogen atom of mercapto benzothiazole has been replaced by a benzoyl group and is generally designated benzo-thiazyl-thio-benzoate.

It is a pale ivory or yellowish powder, with a fineness of 100% through a 30 mesh, has less than 0.5% moisture, a melting point above 115° C., has a specific gravity of 1.43, is soluble in chloroform and benzene, and only slightly soluble in alcohol.

"Ureka C" is suitable under normal conditions. It softens and tends to lump when stored under warm and moist conditions. In general, it may be said that "Ureka C" plus the proper activator can be used in all types of stocks. When activated with guanthal or diphenyl guanidine, it produces excellent tyre, tube, mechanical, footwear and proofing stocks. Used in combination with litharge (this is one of the rare accelerators which can be combined with litharge), or "Oxynone", it imparts excellent electrical properties to the stock. If flat white stocks are desired, this can be obtained by using Ureka C plus a small amount of tetra-methyl-thiuram-mono-sulphide. This last mentioned combination is of value in the preparation of stocks where the vulcanised rubber must come into contact with lacquers.

"Ureka C" plus the proper activator usually requires zinc oxide for activation. Stearic acid should be present in small amounts in gum stocks. If clay or carbon black is used as a filler, better results are obtained, if the amount of stearic acid is increased to 3% based on the rubber content.

"Ureka C" has a plasticizing action on rubber comparable to the chemical materials used specifically for this purpose. This unusual action promotes ease of processing and improves quality by avoiding excessive rubber breakdown or excessive use of softeners.

The Monsanto "*D. P. G.*" is an accelerator of the diphenyl-guanidine type. It is a white powder not darker than the approved colour standard. It shows no residue on 100 mesh screen, its moisture content is less than 0.3%, has less than 0.3% ash, melts above 146° C., its specific gravity is 1.19, it has a strength of not less than 99% by acidimetric titration,

is soluble in alcohol, benzene, chloroform, ether and slightly in water. The diphenyl-guanidine is a very mild accelerator in the absence of zinc oxide, but when the latter is present in amount equal to two or more parts per hundred of rubber, it becomes a very active accelerator. Furthermore, diphenyl-guanidine is not greatly retarded by carbon black or clay, and the temperature at which this accelerator becomes active is from 285° F. upwards. Its activity below 285° F. is so slow that diphenyl-guanidine is not usually used in this range. Formerly "D. P. G." found favour as a tyre and tube accelerator. Today, however, its main use is in moulded mechanical goods. It is also being used now as an activator for the Ureka group.

The Monsanto *Oxynone* is a 2-4 diamino-diphenylamine which appears as a brown crystalline powder with a 99.5% fineness through 100 mesh, and 95% through 200 mesh, without coarse particles, has a melting point of not less than 123° C., ash not over 5%, has a specific gravity of 1.25, is soluble in alcohol, chloroform, benzol, and very slightly in cold water and gasoline.

"Oxynone" is unique in that it acts as an anti-oxidant, anti-plasticizer of unvulcanised rubber, and as an accelerator. The stiffening action of "Oxynone" in uncured stocks can be used to advantage to prevent tubed mechanical stocks from flattening during the process of vulcanisation.

When used alone as an accelerator in rubber, it becomes active at temperatures of 287° F. and above. It is used in wire stocks as a substitute for litharge. It produces a wire insulation which has high electrical

resistance and low leakage values. When used as a substitute for litharge in auto topping stocks, it aids in preserving the varnish from the deterioration of the sun's rays. It is also being used as an activator for Ureka C, and tests show that it retards materially the generation of heat in tyre treads, cushions and other stocks used under similar conditions.

The Monsanto "**A-1**" accelerator is a thiocarbamide. It is a white powder with a fineness of at least 99% through 100 mesh without coarse particles, has no more than 0.5% of moisture, less than 0.5% of ash, its melting point is above 148° C., has a specific gravity of 1.32, and does not show free aniline as uncombined reagents, is insoluble in water and in many solvents but is soluble in alcohol.

"**A-1**" was one of the first organic accelerators known to the rubber industry. It was widely used for a number of years, but has gradually been replaced by the newer accelerators. Today "**A-1**" may be considered as a special purpose accelerator. It is used to some extent in tyre bead stocks and footwear. It is also used to advantage in conjunction with "**R-2 Crystals**" and "**RN-2 Crystals**" to obtain exceedingly fast cures at low temperatures. These combinations of accelerators are welcomed in quick-curing naphta-cements and rubber latex.

The Monsanto "**R-2 Crystals**" is the re-action product of carbon bisulphide with methylene dipiperidine. It is a light brown coarse crystalline solid with a specific gravity of 1.11 and has a melting point of between 50° C. and 60° C.

"R-2 Crystals" is an ultra-accelerator for curing liquid latex, cements etc. It is emulsified readily and like RN-2 Crystals is soluble in the usual rubber solvents, and at low temperatures around 220° F. it approximates the same rate of cure.

The Monsanto "*RN-2*" is the re-action product of carbon bisulphide with methylene di-(N-methyl-cyclohexylamine) blended to a constant curing strength by admixture with a neutral inactive agent. It is a clear brown liquid in which crystals may separate on cooling. These crystals dissolve, however, on slight warming. Its specific gravity is 0.97 and has a flash point at 40° C.

"RN-2" is a liquid form of RN-2 Crystals and has about half the curing strength. It forms emulsions a little more readily than the crystals, but the emulsions are not as stable.

The Monsanto "*RN-2 Crystals*" is the reaction product of carbon bisulphide with methylene di-(N-methyl-cyclohexylamine). It is a light tan coarse crystalline solid with a specific gravity of 1.11 and has a melting point between 55 and 65° C.

"RN-2 Crystals" is an exceptionally fast curing accelerator. It gives excellent cures with low sulphur content and at low temperatures. It is widely used in liquid latex and in fast curing cements. "RN-2 Crystals" is easily emulsified for use in latex compounds. It is readily soluble in naphta, benzol, etc. This property is particularly valuable in cements, as a solution containing "RN-2 Crystals" can be added

directly to a cement containing all the other ingredients, including the sulphur, and thus obviate the necessity of split batch mixings.

The Monsanto "*Pip-Pip*" accelerator is a Piperidine-pentamethylene-dithiocarbamate product. It is a fluffy cream coloured powder with a specific gravity of 1.13. At time of shipment, this accelerator has a fineness of at least 98% through 200 mesh with a melting point over 160° C; but it decomposes slowly in the presence of water, and during storage. It is soluble in alcohol and in solvents.

"Pip-Pip" is an ultra accelerator and will produce short cures at relatively low temperatures. In view of its speed of vulcanisation, it is widely used in liquid latex, fast curing cements etc.

The Monsanto "*R-23*" accelerator is the sodium salt of mercaptobenzothiazole dissolved in water. It is a clear dark brown solution with a specific gravity of 1.23 to 1.26 at 20° C. The solution contains 48 to 52% of the sodium salt of mercaptobenzothiazole, calculated by the regular mercaptobenzothiazole analysis. "*R-23*" can be added to liquid latex, but is relatively slow in its action in latex when used alone. When it is used, however, in conjunction with RN-2 Crystals R-2 Crystals, or Pip-Pip in latex, the combined acceleration is very powerful and fast curing excellent cures can be obtained in a short time at low temperatures.

"*El-Sixty*" is another of Monsanto's accelerators. It is a di-benzothiazyl-dimethylthiol urea with the following specifications and properties:—

A light cream coloured powder the fineness of which is at least 99.5% through a 200 mesh, with no coarse particles; has a moisture less than 1%; ash less than 0.7%; its melting point is not less than 220° C., and its specific gravity is 1.29.

The accelerator's value and its delayed action are equivalent to that of the accepted standard. It is very slightly soluble in acetone, alcohol and chloroform and slightly soluble in hot pyridine or orthodichlor benzene.

"El-Sixty" was developed as an accelerator for high clay stocks. This feature of the material has made it the outstanding accelerator for all types of mechanical goods, including heels, soles and general moulded articles.

This accelerator may be activated with Guantal, D. P. G. or any Amine type accelerator for use in tyre, tube stocks and the like, and even when activated, it produces stocks which are easy to process and show little scorching tendency under severe conditions.

"El-Sixty" has also found favour in latex work, when it is used in conjunction with accelerators such as RN-2 Crystals or Pip-Pip.

The Monsanto "*Guantal*" is the salt or ester formed by reacting two molecules of diphenyl-guanidine and one molecule of phthalic acid and contains one-half mole of water of crystallization. The specifications and properties of this accelerator are as follows:—

It is a white powder ranging from blue-white to faint grey. Its fineness is at least 99.5% through a 200 mesh with no coarse particles; has no more than 3% of moisture, and this amount is found in the hydrate; has less than 0.5% ash; its melting point is

not below 178° C, and has a specific gravity of 1.20. It is soluble in alcohol and insoluble in benzene and gasoline.

“*Guantal*” is used primarily as an activator of the “Ureka” type of accelerators. When used in a fixed ratio with 2-4 Dinitro Phenyl Thio Benzothiazole and Diphenyl Guanidine, good results are obtained. When “*D. P. G.*” is used as an activator of Ureka C., in tyre carcass stocks for example, it is necessary to limit the amount of D. P. G. due to processing problems, which are liable to arise if the D. P. G. content is high, whereas with a lower D. P. G. content, the Ureka C content is high, and the resulting stocks tend to stiffen considerably on ageing. This is particularly true of lorry tyre carcass stocks subjected to high heat conditions during service.

With Guantal as an activator for Ureka C, increased amounts of Guantal and decreased amounts of Ureka C can be used with safety during processing, and lorry tyre stocks using this combination of accelerators give excellent service on the road.

The Monsanto “*Santocure*” is a condensation product of mercapto benzothiazole with cyclohexylamine and is a light tan or buff coloured powder with a fineness of at least 99.5% through 200 mesh. After being dried for six hours at 70° C. under high vacuum, its moisture does not exceed 0.5%. It has a melting point above 90° C., and a specific gravity of 1.27.

Santocure exhibits a remarkable delayed action on cure and yet is a powerful accelerator. When it becomes active, Santocure produces its own activator. This is unique for an accelerator having such a pronounced delayed action.

In the normal curing ranges, the amount of acceleration can usually be cut in half when using Santocure. This is true in stocks containing a high percentage of carbon black as well as pure gum stocks, in which it produces high modulus.

The delayed action of Santocure is so pronounced that often the use of an activator is indicated. In that case *Guantal, D. P. G.* or any of the *Amine* type may be used. Except that Santocure discolours white stocks to some extent, its use is practically unlimited in its application to various types of rubber compounds.

Monsanto says—and we can confirm it by our experience—that when used alone “*Santocure*” is quite inert at low temperatures and exhibits more delayed action and less pre-curing than any other organic accelerator. Under the influence of time and temperature it breaks down into its components to form a remarkably fast and strong accelerator. The modulus and tensiles produced by that accelerator are exceptionally high, particularly in lightly loaded stocks.

Its ability to produce its own activator or secondary accelerator is unique among rubber vulcanization accelerators. It is capable of further activation by guanidines, aldehyde amines, thiurams and some inorganic substances. When used in conjunction with certain accelerators of the mercapto type, the rate of cure can be speeded up considerably. The physical properties of compounds cured with these mixtures are, however, simply an additive result of the two accelerators. This activity with many kinds of secondary accelerators increases its utility and makes possible its advantageous use in almost all kinds of rubber articles.

When consistent with the available curing time and temperature, "**Santocure**" will undoubtedly give the best results if used alone. For general purposes, however, activation with D. P. G. is excellent. While its accelerating ability is quite slow in developing at low temperatures, this ability comes into play very quickly at what might be called normal curing temperatures. For example, a gum stock containing on the rubber 5 parts of zinc oxide, 3 parts of sulphur and 0.36 parts of "**Santocure**" activated by 0.24 parts of D. P. G. shows no cure in 20 minutes at 20 pounds steam. In 5 minutes at 60 pounds steam the tensile is 4400 pounds and the cure is but little short of optimum. The processing advantage and lack of pre-curing tendency of "**Santocure**" is obvious, however, it must be noted that this great difference in curing rate between high and low temperatures is more pronounced in a gum-type compound than in one containing the usual ingredients such as carbon black, whiting etc.

Of interest is the economy of "**Santocure**." When acceleration of this type is desirable, a considerable saving in acceleration cost can usually be expected. In many cases this saving is accompanied by an improvement in quality and a greater margin of processing safety. We give hereafter a few test-results with "**Santocure**" combined with other accelerators.

**"Santocure", "El-Sixty and "Ureka C"
in a Gum Stock.**

Base Formula.			
Smoked Sheets	100.	A—"Ureka C"45
Zinc Oxide	10.	"Guantal"30
Sulphur	3.	B—"El-Sixty"525
Stearic Acid75	"Guantal"225
	<hr/>	C—"Santocure"45
	113.75	D—"Santocure"38
		D. P. G.16
		E—"Santocure"31
		D. P. G.31

	Cure	300 %	500 %	Break	Elong.
A	15/30 lbs.	250	600	3000	800
B		230	560	2700	785
C			No Cure		
D			No Cure		
E		270	625	3060	775
A	30/30 lbs.	335	850	4065	775
B		350	905	3910	760
C		180	345	1985	835
D		390	1100	4500	730
E		425	1380	4700	720
A	45/30 lbs.	375	1000	4200	730
B		415	1190	3700	700
C		380	1115	3750	700
D		475	1510	4150	670
E		500	1590	4110	660
A	60/30 lbs.	380	1025	3990	750
B		420	1115	3650	690
C		435	1125	3650	690
D		480	1440	3960	680
E		510	1565	3700	640

	Cure	300%	500%	Break	Elong.
A	90/30 lbs.	390	915	3530	730
B		420	1100	3430	700
C		430	1035	3600	700
D		460	1345	3900	680
E		485	1400	3580	655

**“Santocure”, “El-Sixty” and “Ureka C”
in a Carbon Black Compound.**

Base Formula.			
Smoked sheets 100.	A — “Ureka C”	.68
Zinc Oxide 5.	“Guantal”	.45
Carbon Black 45.	B — “El-Sixty”	.79
Stearic Acid 3.25	“Guantal”	.34
Pine Tar 2.	C — “Santocure”	.66
Sulphur 3.	D — “Santocure”	.53
		E — “Santocure”	.56
	158.25	D. P. G.	.24

	Cure	300%	500%	Break	Elong.
A	15/40 lbs.	1145	2700	3840	640
B		1115	2660	3740	630
C		1350	3200	4500	635
D		1020	2560	3870	640
E		1440	3460	4700	640
A	30/40 lbs.	1600	3610	4655	615
B		1710	3760	4425	580
C		1880	4000	4880	600
D		1560	3475	4520	615
E		1940	4130	4780	585
A	45/40 lbs.	1940	4000	4480	580
B		1955	4125	4620	555
C		2020	4120	4615	560
D		1815	4020	4580	580
E		2140	4500	4800	555

	Cure	300 %	500 %	Break	Elong
A	60/40 lbs.	1960	4210	4485	540
B		2070	4250	4350	510
C		2155	4400	4400	500
D		1850	4050	4520	575
E		2140	4320	490
A	90/40 lbs.	1920	4160	4160	500
B		2080	4085	490
C		2070	4360	4360	500
D		1850	3955	4200	540
E		2000	4200	4200	500

In these tests, "SANTOCURE" alone is shown to be a very powerful accelerator in a compound containing Carbon Black. Used with D. P. G. as in the "E" stock, the rate of cure is of course increased considerably.

"Santocure" in Bicycle Tyre Stocks.

			Tread	Carcass
Smoked Sheets	100.	50.
Pale Crepe	50.
Zinc Oxide (Fast Curing — Mixed Particle)	5.	5.
Clay	70.	15.
Whiting	50.	60.
Paraffin	1.	1.
Stearic Acid	1.	1.
Red Oxide	6.
Sulphur	2.	2.
Santocure625	.625
D. P. G.625	.625

236.250 185.25

			Tread		Shore	
Cure			300%	Break	Elong.	Hardness
2	Min.	@ 70 lbs.	1605	2630	480	61
4	"	" 70 "	1715	2815	495	65
6	"	" 70 "	1770	2775	455	67
9	"	" 70 "	1600	2670	450	67

			Carcass			
Cure			500%	Break	Elong.	
2	"	" 70 "	2220	3330	600	
4	"	" 70 "	2375	3070	575	
6	"	" 70 "	2330	2900	560	
9	"	" 70 "	2250	2800	560	

These compounds indicate the high modulus and tensile obtainable with "SANTOCURE"—D. P. G. combinations. Both stocks are fast curing but non-scorchy.

"Santocure" in a Moulding Compound.

Base Formula			
Smoked Sheets	40.	
Whole Tyre Reclaim		120.	
Zinc Oxide	5.	A—"Santocure" .625
Clay	...	40.	D. P. G. .625
Whiting	...	100.	
"Cycline Oil"	5.	B—"El-Sixty" 1.15
Stearic Acid	1.25	D. P. G. .40
Sulphur	...	2.5	
			313.75

	Cure	Break	Elong.	Shore Hardness
A	5 Min. @ 65 lbs.	950	255	75
B	5 Min. @ 65	915	265	75
A	7 Min. @ 65	930	255	77
B	7 Min. @ 65	935	275	76
A	9 Min. @ 65	950	250	77
B	9 Min. @ 65	960	270	77
A	12 Min. @ 65	875	230	76
B	12 Min. @ 65	875	240	76

In this type compound "SANTOCURE"—D. P. G. compares very well with "EL-SIXTY"—D. P. G., which is excellent for cheap loaded stocks. The "SANTOCURE" stock is slightly safer so far as scorch is concerned.

"Santocure" "El-Sixty" in a Moulding Compound.

Base Formula.

Smoked Sheets	77.
Tube Reclaim	38.
Zinc Oxide	3.75
Whiting	50.
Soft Black	62.
Stearic Acid	1.
"Santoflex B"75
Sulphur	2.3125
			<hr/> 234.8125

	A	B	C	D	E
"Santocure"	.625	.3125	.375
"D. P. G."3125	.375	.25	.25
"El-Sixty"75	.875

	Cure	300 %	Break	Elong.	Shore Hardness	Shore Elasticity
A	4 Min. @ 70 lbs.	1340	2180	485	64	83
B		1370	2300	460	64	83
C		1420	2380	485	64	83
D		1300	2200	475	64	83
E		1350	2270	490	66	84
A	6 Min. @ 70 lbs.	1360	2110	470	66	83
B		1380	2130	470	66	83
C		1420	2105	440	66	83
D		1400	2290	485	66	83
E		1440	2250	470	66	82
A	8 Min. @ 70 lbs.	1335	2010	440	65	82
B		1440	2125	440	65	82
C		1460	2020	430	65	82
D		1390	2275	475	65	82
E		1500	2150	450	65	82
A	10 Min. @ 70 lbs.	1335	2080	435	65	82
B		1350	2220	475	65	82
C		1435	2075	450	65	82
D		1460	2040	420	65	82
E		1460	2080	420	65	82

The "B" compound, in which acceleration cost is very low, gives good results. All the compounds are practically scorch-free with the possible exception of "E".

“Santocure” in a Sponge Compound.

Base Formula.

Clean Thin Brown*	90.		
Tube Reclaim	17.	
Zinc Oxide	5.	
Mineral Rubber	10.	A—“Santocure”75
Oleic Acid	10.	B—“Santocure”5
Stearic Acid	4.	D. P. G.375
“Cycline Oil”	25.	C—“Santocure”75
Whiting	36.	Thiurad03125
Paraffin	1.25	Cure: 20 to 25 Min.
Soda	10.	@ 60 lbs. 1" Thickness.
Sulphur	...	3.375	

211.625

In this type of sponge mix any one of the above accelerations gives good results. The rate of cure, which, of course, has a great influence on the cell structure and “skin” formation, can be varied over a wide range with “SANTOCURE” acceleration. Higher amounts of accelerator than those shown above can be used successfully in order to shorten curing times. The remarkable delayed action of “SANTOCURE”, even in combination with D. P. G., is still sufficient to obtain good blowing. A further advantage of “SANTOCURE’S” delayed action is in moulding intricate shapes. It is often found that these shapes can be moulded without the necessity of using a compound which requires more than a normal time to reach optimum cure.

*This is an alternative to Pale Crepe or Smoked Sheets. It is a slightly softer cheaper grade of rubber and requires less mastication on the mixing roller. This grade of rubber is widely used in America, and, if it is not available, the same result can be obtained by the use of ordinary rubber twice masticated as suggested under “Sponge Rubber”, Chapter XII, Vol. I.

“Santocure” in a Compound with High Soft Black Content.

Base Formula.

Smoked Sheets	100.			
Zinc Oxide	5.	A—“Santocure”72	
Soft Black ...	150.	B—“Santocure”63	
“Cycline Oil”	2.5	C—“Santocure”52	
Stearic Acid	1.	D—“Santocure”52	
“Flectol H”	1.	D. P. G.013	
Sulphur	2.5			
	262.0			

Cure	300%	Break	Elong.
A 10 Min. @ 50 lbs.	1130	2000	480
B	1065	2000	480
C	980	1745	485
D	1060	1830	485
A 20 Min. @ 50 lbs.	1100	1850	470
B	1090	1815	490
C	1085	1830	485
D	1100	1770	490
A 30 Min. @ 50 lbs.	1070	1640	475
B	1035	1640	485
C	1000	1530	490
D	1040	1500	465
A 40 Min. @ 50 lbs.	1060	1620	475
B	1040	1680	490
C	1030	1610	490
D	1040	1670	490

At full cure there is little difference in physical properties. All of the compounds are safe handling.

"Santocure" in a Black Heel Type Compound.**Base Formula.**

Smoked Sheets	50.	A—"El-Sixty"	1.45
Whole Tyre Reclaim	25.		"Guantal"70
Tube Reclaim	... 60.		B—"Santocure"92
Mineral Rubber	... 6.		C—"Santocure"72
Stearic Acid 1.50		D—"Santocure"60
Carbon Black 32.		E—"Santocure"57
Hard Clay 50.		D. P. G.40
"Flectol H"75		F—"Santocure"57
Zinc Oxide 5.		"Guantal"40
Sulphur 3.50		H—"Santocure"50
	-----		D. P. G.50
	233.75		K—"Santocure"50
			"Guantal"50

	Cure	300 %	Break	Elong.	Shore Hardness
A	3 Min. @ 60 lbs.	1300	1760	405	65
B		1490	2040	405	65
C		1200	1840	440	65
D		1160	1780	440	64
E		1420	2000	405	64
F		1220	1770	435	64
H		1320	1870	410	64
K		1190	1720	430	64
A	6 Min. @ 60 lbs.	1540	1905	385	69
B		1680	2090	380	69
C		1525	1960	395	67
D		1360	1800	400	66
E		1625	2090	390	66
F		1550	1980	295	66
H		1610	1960	370	68
K		1500	1920	390	69

	Cure	300%	Break	Elong.	Shore. Hardness
A	9 Min. @ 60 lbs.	1760	2000	360	71
B		1705	2000	350	71
C		1580	1900	380	71
D		1460	1875	390	66
E		1750	1980	350	69
F		1630	2000	380	71
H		1720	2020	370	71
K		1620	1940	370	71
A	12 Min. @ 60 lbs.	1870	1940	315	72
B		1730	2040	355	73
C		1620	1960	380	72
D		1480	1840	385	69
E		1705	1920	345	71
F		1680	1940	360	71
H		1700	1940	350	71
K		1640	1790	340	71

The compounds containing "SANTOCURE" and D. P. G. give about the same scorch test results as the "A" stock. The compounds containing "SANTOCURE" and "GUANTAL" are less scorchy and of course the straight "SANTOCURE" stocks are the safest. All can be processed very easily.

"Santocure" in a Red Heel Type Compound.

Base Formula.

Smoked Sheets	...	73.5		
Red Tube Reclaim		44.		
Stearic Acid	1.5		
Witco 20*	6.5	A—"El-Sixty"80
Mineral Rubber	7.5	D. P. G.80
Lime6	B—"Santocure"625
Red Oxide	1.8	C—"Santocure"44
"Flectol H"9	D. P. G.44
Zinc Oxide	5.	D—"Santocure"37
Hard Clay	120.	D. P. G.37
Sulphur	3.5		
264.8				

	Cure	300%	Break	Elong.	Shore Hardness
A	3 Min. @ 60 lbs.	720	1025	405	48
B		Did Not Cure			
C		750	1190	420	52
D		600	1025	470	46
A	6 Min. @ 60 lbs.	1100	1590	400	54
B		910	1670	440	54
C		1200	1830	420	60
D		1070	1690	400	56
A	9 Min. @ 60 lbs.	1255	1705	400	60
B		1090	1705	440	60
C		1220	1820	410	64
D		1135	1815	415	60

* Witco 20 is a product similar to Pine Tar, Tackol, or any other softener.

Cure	300 %	Break	Elong.	Shore Hardness
A 12 Min. @ 60 lbs.	1300	1770	390	62
B	1080	1760	440	62
C	1300	1870	440	65
D	1130	1850	425	62

Scorch tests show that the "B" compound is the safest and the other three are about the same. All will process satisfactorily.

"Santocure" in Medium Quality Extruded Compound

Base Formula

Smoked Sheets 57.	A—"El-Sixty" 1.00
Tube Reclaim 72.	D. P. G.25
Brown Factice * 14.5	B—"Santocure"70
Zinc Oxide 4.5	C—"Santocure"57
Thermax 72.	D—"Santocure"45
Stearic Acid 1.	E—"Santocure"34
"Flectol H" 1.	D. P. G.23
Sulphur 2.5	F—"Santocure"40
	<hr/> 224.5	"El-Sixty"40

* Brown Factice should be used in this formula as the use of white Factice requires the addition of lime or an alkali material sufficient to neutralise the acidity of the White Factice produced during vulcanisation, whereas Brown Factice does not develop such acidity.

Cured in Open Steam

	Cure	300%	Break	Elong.	Shore Hardness
A	5 Min. @ 50 lbs.	1000	1910	495	56
B		960	2000	520	55
C		865	1975	560	55
D		750	1730	555	53
E		780	1900	600	54
F		930	2090	560	56
A	10 Min. @ 50 lbs.	1280	1975	460	58
B		1185	2150	490	58
C		1110	2120	500	58
D		1025	1980	500	56
E		1035	1950	495	55
F		1060	2000	490	58
A	15 Min. @ 50 lbs.	1290	2115	480	60
B		1200	2100	490	60
C		1120	2065	490	58
D		1070	2070	500	56
E		1105	1960	485	56
F		1200	1975	490	58
A	20 Min. @ 50 lbs.	1300	2000	430	60
B		1250	2000	470	60
C		1230	2000	480	59
D		1150	1910	490	56
E		1155	2100	495	56
F		1220	1900	440	59

The compounds containing "SANTOCURE" alone are less scorchy than any of the others but cure rapidly enough to prevent deformation at the start of the cure. All are very safe handling.

Santocure Combination and The Continuous Vulcanisation Process.

Santocure, in combination with other accelerators, can readily be adapted to either the press-curing process or the *continuous vulcanisation process*, both of which are employed in the manufacture of insulation or jacket stocks, by Wire and Cable manufacturers, when high modulus and tensile are specially desirable.

The continuous vulcanisation process is done at very high temperatures, say in the neighbourhood of 200°C , and is already widely adopted in America for the manufacture of extruded cables and wires, particularly for the thin-walled types. Evidently, the continuous vulcanisation process is more economical and tends to faster production rates. The actual curing time is only a matter of seconds, or at the most $1\frac{1}{2}$ minutes, depending more upon the thickness of the rubber layer to be vulcanised than upon the amount of accelerator present in the mix. But considerable care is necessary, however, in the selection of a properly balanced type of accelerator, so that scorching in the extruder may be avoided, whilst still maintaining sufficient speed of cure to get the article vulcanised in the 100-ft. vulcaniser used for such kind of cure. It would be interesting to consider whether there would be any reason why we should not vulcanise rubber hoses, built on aluminium mandrels, or rubber sheetings, with or without insertion, conveyed through the vulcaniser upon an endless conveying table of open woven asbestos fabric. Evidently, for such fabrication, an open steam vulcaniser is out of the question, as it is

impossible to get a continuous vulcanisation in open steam. It might, perhaps, be possible in a steam jacketted vulcaniser, but the difficulty would then be to obtain the required temperature of, say, not less than 388° F. Consequently the best type of vulcaniser will thus be one electrically heated having a certain number of resistances, to be switched on, or off independently according to the required temperature. Such vulcaniser can be made of three layers, an outside layer of strong wood, an intermediate layer of asbestos, and an inner layer of copper. On the walls, there should be several openings of 1" diameter, to facilitate the circulation of air inside the apparatus, where a conveying table of open woven asbestos fabric should run on copper rolls. The wires, the rubber hoses, or the sheeting, as the case may be, should enter the vulcaniser on one side and leave it at the opposite side conveyed on the asbestos conveying table, run through the vulcaniser at a rate of from 300 to 600 ft. per minute, the time depending upon the thickness of the rubber layer to be vulcanised. To facilitate increased production, rubber sheetings should be prepared in advance in rolls of 600 ft. or longer. With regard to rubber hoses, they should be built on aluminium mandrels joined together end to end by means of a simple plug-type detachable joint in the same way as bicycle tubes are produced on mandrels, through the right angle head of the tubing machine (Fig. XIII, page 154, Vol. I). It is understood the speed of conveying the goods to be vulcanised through the electrically heated vulcaniser should be regulated by a mechanical device, which could be easily constructed, and the apparatus should be provided with a sufficient number of thermometers to check the temperature inside the vulcaniser.

The following few formulas give characteristic acceleration and illustrate combinations which might be adapted by slight changes to any specific factory conditions:—

Brown Wire Jacket Stock.

(Continuous Vulcanisation.)

Smoked Sheets	43.000
Zinc Oxide	4.000
Hydrated Alumina, Grade C741 *		10.000
Whiting	31.375
Lithopone	5.000
Red Oxide	4.000
Soft Black	0.6875
Flectol H	0.250
Sulphur	0.6875
Santocure	0.375
El Sixty	0.4375
		<hr/> 99.8125

Cures at 388° F.

20 Seconds.			25 Seconds.			30 Seconds.		
200%	Break	Elong.	200%	Break	Elong.	200%	Break	Elong.
560	2685	550	515	2550	555	455	2200	525

After 96 hours in Oxygen Bomb (70° C, 300 lbs. oxygen pressure)

650	2300	540	660	2180	530	610	1975	490
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*When Hydrated Alumina Grade C 741 is not available, China Clay or a combination of Zinc Oxide in large concentration with talc can be used, and in this case the proportion of the latter can be increased.

This stock is not scorchy and should process easily in the factory. In conclusion, when Santocure is used in combination with El-Sixty as shown in the above formula, it should give excellent results.

Ivory Wire Jacket Stock.

(Continuous Vulcanisation)

Smoked Sheets	43.000
Zinc Oxide	10.000
Whiting	38.000
Lithopone	8.000
Yellow	0.125
Flectol H	0.250
Sulphur	0.750
Stearic Acid	0.3125
Santocure	0.4375
Guantal	0.375
		<hr/>
		101.2500

Cures at 388° F.

20 Seconds.			25 Seconds.			30 Seconds.		
200%	Break	Elong.	200%	Break	Elong.	200%	Break	Elong
428	2200	500	433	2250	500	455	2320	520

After 96 hours in Oxygen Bomb (70° C, 300 lbs. oxygen pressure)

700	2030	500	680	2100	500	625	2000	480
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A green jacket may be obtained with the above formula by replacing 1.5 parts of whiting with 1.5 parts of green. Further the above formula illustrates how a combination of Santocure and Guantal can be used in the continuous vulcanisation process.

Telephone Wire

(Continuous Vulcanization)

Smoked Sheets	27.000
Boot & Shoe Reclaim	12.000
Mineral Rubber	4.000
Lithopone	8.000
Whiting	37.500
Stearic Acid250
Zinc Oxide	9.000
"Flectol H"625
Sulphur	1.500
"Thiurad"0625
"Santocure"	1875

100.1250

Yield Values on Compression Tester:

Samples on $\frac{18}{10}$ Bronze tinned conductor with wall of .022 inches.

Cure at 388°F	Original	Aged in Oxygen Bomb	
		48 hours	96 hours
15 Seconds	1260	1260	1150
20 Seconds	1300	1170	1050
25 Seconds	1310	1150	1030

These figures were obtained by insulating wire in the laboratory and curing later in the quick-curing apparatus. It is believed that results comparable to the 15-second cure can be obtained in the factory at a speed of 600 feet per minute using a 100 foot tube at the same temperature. This stock is not at all scorchy, as it shows no change in plasticity figures after 3 hours cure at 200°F.

Monsanto says that the figures shown for the three compounds given above represent laboratory experiments. Those for stocks to be processed by the continuous vulcanisation process were determined by tests in the laboratory quick-curing apparatus. It must be remembered, however, that in the laboratory the samples of raw stock are at room temperature at the beginning of the cure instead of at the extrusion temperature as in the case of actual factory production. This lag in laboratory cure is difficult to evaluate, but it is probable that several seconds should be deducted from the laboratory cure to make it comparable to the factory cure. If a stock cures satisfactorily in 20 seconds in the laboratory, it is probable that the same stock may cure at the same temperature in the factory at the rate of 400 feet per minute in a 100-ft. vulcaniser. This cannot, however, be a general rule, since wall thickness and construction, in the case of wires with cotton layers, play an important part in determining the cure in the factory.

The Monsanto "Aldehyde Amine Accelerators."

Those interested in the vulcanisation of rubber have, for a long time, been familiar with accelerators derived from aldehydes. Hexamethylene tetramine is a reaction product derived from formaldehyde and ammonia. Aldehyde ammonia is secured by reacting acetaldehyde and ammonia. These compounds are definite and, for all practical purposes, are the only products resulting from the action of ammonia on these aldehydes.

When we turn to the organic bases, says Monsanto, and particularly to the aromatic amines, a definite rule is no longer operative. The product secured from the

reaction of an aldehyde and an amine will now vary, depending on the conditions under which the reaction is brought about. The relative quantities of reacting substances, their temperature, the presence of small quantities of impurities, or added reagents, all have their effect which tends to increase the number of products all of which differ in appearance, in physical and chemical properties, and in accelerating effect.

For example, formaldehyde reacts with aniline under different conditions to give at least three different products. Equal molecular quantities of formaldehyde and aniline react to form methylene aniline which is a solid with a melting point sufficiently high that it may be ground. Its colour is yellowish white. Two molecular quantities of aniline react with one molecular quantity of formaldehyde to produce the substance known as methylene diphenamine, or methylene dianilide. This material, made commercially, is yellow to brown in colour. Its melting point is much lower than that of methylene aniline and it may be converted, by an interior rearrangement brought about by heat, to para amido benzyl aniline which is a solid with a very low melting point.

The reactions of acetaldehyde and aniline are much more complex and the products larger in number than those obtained from formaldehyde and aniline. The simple products have been known for years and have been classed as Schiff's bases—taking this name from Hugo Schiff who conducted extensive investigations in aldehyde-amine reaction products many years ago. Ethylidene dianilide results from two molecular proportions of aniline reacting with one molecular proportion of acetaldehyde. Ethylidene aniline is produced when equal molecular quantities of acetaldehyde and aniline react. The preparation of

both these substances, however, requires very careful attention to details. Temperatures, solvent employed, etc., must be carefully studied and the procedure adopted must be religiously adhered to. The records of Schiff, Eibner, Eckstein and many others are replete with instructions and details to be followed if crystalline products are to be obtained.

The large field of non-crystalline materials which later was to furnish a fruitful field for the development of accelerators was avoided then because of the natural inclination of investigators to work with the more attractive crystalline materials.

The use of formaldehyde-aniline reaction products as accelerators was proposed several years ago by Bastide. The assumption that similar products derived from acetaldehyde and aniline would be accelerators is, of course, no novelty. In fact, we find that Bastide himself recognized this and mentioned it in his patent. Others have also been interested in the accelerating value of these products, but all of them confined their efforts to the products similar to methylene aniline and methylene dianilide, namely ethylidene aniline and ethylidene dianilide. None of the previous investigators even suspected the existence of higher reaction products and, of course, they had no knowledge of the fact that these materials are much more desirable accelerators than simple ethylidene aniline. Furthermore, they were entirely unaware of the advantage of using two or more aldehydes at different stages in the reaction.

These higher reaction products are, in the main, resins or liquids of high viscosity and are produced by varying the conditions of reaction. It may be said without exaggeration that within this class of compounds

nearly every degree of acceleration and temperature that may be desired, is obtainable. Approximately one hundred accelerators, all belonging to this class, are known today. Many more undoubtedly exist.

Monsanto is producing a few members of the series they have selected because of their graded accelerating effect. But due to their highly complex nature, no attempt has been made to name them chemically. They therefore, have been given trade names, which are sufficient for all practical purposes.

"A-10" is one of these accelerators. It is a condensation product of aniline and formaldehyde, is neither methylene dianilide nor formaldehyde aniline, but probably a mixture in which the latter product predominates. It is a white or yellowish tinted powder, with 95% fineness through 200 mesh and 99% through 100 mesh; it has less than 5% loss on heating, when heated for two hours at 105° C., its melting point starts at 120° C. It has a specific gravity of 1.17, does not possess any excess of free aniline and shows not more than traces of formaldehyde.

"A-10" tends to become brownish coloured on exposure to light and heat. It is insoluble in water and its accelerating value is very mild. Because of this mild accelerating effect, "A-10" is not generally used today as an accelerator, but advantage is taken of this property, however, in stocks such as air bags, where often a slow-curing low modulus compound is desired. It finds its greatest use as a plasticizer and activator of other accelerators. As "A-10" has a large percentage of formaldehyde reacted with aniline, its use as an activator for other accelerators is to be preferred to products of the same type which contain less.

"A-11". This is another accelerator of the same series. It is a specially processed formaldehyde derivative of a condensation product of aniline and acetaldehyde and as such is of a complex chemical composition. It is a brown resinous powder with a melting point between 75° and 85° C., and has a specific gravity of 1.15. Its acceleration value is greater than that of A-19, particulars of which appear in later pages. In fact "A-11" is an accelerator similar in composition and physical properties to A-19, and can be substituted by the latter, when used in equal quantities, as it gives then a more rapid cure. Finally, all of the excellent ageing qualities found in A-19 are retained in "A-11".

"A-16" is chemically, an aldehyde reaction of Schiff's base. More specifically, it is an aldehyde reaction product of a molecularly rearranged and polymerized aldehyde amine, in which two different aliphatic aldehydes and aniline are the basic materials.

"A-16" can also be regarded as a further development in the series of aldehyde accelerators, the most notable types of which are the A-11 and A-19.

As an aid to vulcanisation, "A-16" displays unusual merit. It has many advantages not shown in other accelerators. These may be briefly summarised as: whilst "A-16" is a normally handled material, it imparts tensile strength comparable to ultra-accelerators; it gives an unusually long range of useful cure, provides the best of ageing, even on overcure, and is suitable for practically all types of compounds. "A-16" stocks show no reversion on overcure, neither do they stiffen materially under the same conditions. No doubt,

this very uniform degree of hardness over a wide range of cure is a most desirable feature.

While "A-16" is easily handled, it is, nevertheless, a most powerful vulcanising accelerator and produces tensile strengths in considerable excess of 4000 lbs. per sq. inch, even in pure gum stocks. Good cures are obtained in a few minutes at either 40 lbs. (287° F.) or 30 lbs. (274° F.) of steam. "A-16" will give equal results in a longer time at 20 lbs. (259° F.) steam, but when the temperature is reduced much below this point, the time factor is prolonged beyond normal factory practice.

Physically, "A-16" is a thin brown liquid, very mobile at all normal room temperatures. It will pour quickly out of any container and no time is required for draining. The container need not even be warmed at any time. The "A-16" accelerator, as it appears, consists of two-thirds active material and one-third high boiling inert liquid diluent. This dilution is said to convert "A-16" into such physical shape that will allow of ease in handling. The "A-16" base alone is a viscous sticky material, having a tendency to adhere to the mill rolls, but the accelerator is quickly absorbed by the rubber. So, if added near the centre of the batch, it is all absorbed before any has a chance to run over to the roll guides. "A-16" may be master-batched in the usual way, although this is not necessary, and because of its physical nature, one should not attempt more than a 10% master-batch.

"A-16" may be safely handled in the factory as it is non-toxic and gives no form of cyanosis or skin rash. Because of its colour, it darkens white or light coloured stocks. However, unless a pure white or a very

brilliant colour is desired, A-16 may well be used in all types of compounds.

Zinc Oxide is a necessary catalyst with "A-16" as well as most other organic accelerators. Without it, the accelerator shows considerable activity, but does not attain its full strength until about two parts of zinc oxide are present in 100 parts of rubber. To overcome varying conditions, it is suggested to use five parts of zinc oxide to 100 parts of rubber in all A-16 formulas.

Carbon Black retards "A-16" materially. By increasing the amount of accelerator, however, the retardation is overcome and very good stocks result.

Clay also retards "A-16", but not nearly as much as Carbon Black. Relatively slight variation in compounding will equalize these stocks. The addition of *lime* makes "A-16" stocks more scorchy and yet does not appear to help the full cure. The same is true of *magnesia* in a more pronounced degree, and of *litharge* to a lesser degree. The addition of any mineral accelerator to "A-16" stocks is therefore, not recommended. Softeners, such as pine tar, fluxol and rosin, all retard "A-16", and in compounding, proper allowance should be made for any considerable amount of such softeners. *Stearic Acid* in the concentration of 1% of rubber, seems to be quite neutral, and because of the possibility of deficiency of organic acids in certain rubbers, the use of stearic acid in "A-16" compounds is recommended, particularly where off-grade rubbers are used. We, therefore, suggest about $\frac{1}{2}$ % stearic acid with all high grade rubbers and $1\frac{1}{2}$ % with all wild or low grade plantation rubbers.

"A-19" is also a formaldehyde derivative of a condensation product of aniline and acetaldehyde like A-11. It is a brown resinous powder with a melting point between 75° and 85° C., and has a specific gravity of 1.17.

This accelerator is insoluble in water and non-hygroscopic; its acceleration value has been found to be unaffected by several types of storages under normal conditions. The low melting point of "A-19" is a great asset in the mixing process, since the accelerator melts on the mill and dissolves in the rubber. This insures its thorough dispersion in the mix. One of the outstanding features of "A-19" is the excellent ageing qualities it imparts to rubber stocks. Numerous tests, run over a period of years, have shown A-19 compounds to age considerably better than any of a large number of other accelerators. Under the circumstances, this accelerator is perhaps the most widely used of those forming the aldehyde group, with the exception probably of "A-16".

In any case, "A-19" produces excellent stocks in any type of rubber compound, where the use of an aldehyde accelerator is desirable.

"A-32" accelerator is a reaction product of butraldehyde and butylidene aniline. It is a red yellow to orange brown oily liquid which is slightly turbid when cold. Its specific gravity is 0.98, has a flash point at 80° C., and is soluble in benzene, chloroform, acetone and solvent-naphta.

"A-32" is the highest modulus and highest tensile accelerator of any of the aldehyde amine group herein described. In most stocks it gives excellent cures when

used in relatively small amounts. It is well suited for the manufacture of tyres, tubes and, in general, of all mechanical goods. It is also used to advantage in certain types of dry-heat-stocks and is of particular advantage in soles and heels, lining, gum and friction stocks.

“**A-77**” is still another of these accelerators. It is the condensation product of acetaldehyde and aniline obtained in the Monsanto laboratory. Such products, known as Aldehyde-derivatives of Schiff's bases, are of complex chemical composition. It is a free-flowing reddish-brown liquid with a specific gravity of 1.04, a flash point at 55° C., is soluble in benzene, chloroform and acetone and partly soluble in alcohol and gasoline.

“**A-77**” is used extensively, at the present time, as an accelerator for ***Ebonite Articles***. The characteristic of this accelerator to produce low tensile low modulus stocks makes it ideal for producing an ebonite which is tough, flexible, and not brittle. It is used in the manufacture of ebonite automobile steering wheels, battery cases, and the like.

“**A-77**” is retarded by carbon black and clay, but is unaffected by the other ordinary minerals used in rubber compounds. As both magnesium oxide, and lime, cause marked softening down on long cures, these chemicals should not be used in conjunction with this accelerator.

“**A-100**” is an Aldehyde-derivative of a Schiff's base made with the use of both butraldehyde and acetaldehyde. It is a dark red brown oily liquid

with a specific gravity of 1.04. It has a flash point at 85° C. and is soluble in benzene, chloroform, acetone and solvent-naphtha.

"A-100" is a special blend of aldehydes with aniline to produce, like A-77, short cures in **ebonite stocks**. It was introduced a number of years ago, and immediately filled a need of the industry. Since then, it has continued to find favour in application such as battery cases, steering wheels, and all sorts of ebonite moulded goods.

The accelerator "*Thiofide*" is dibenzthiazyl-disulphide. It appears commercially as a light yellow powder of melting point from 160°-165° C., and having a specific gravity of 1.50. In common with the other non-resinous types of accelerators, it is ground so that essentially all will pass a 200 mesh screen. It is entirely non-toxic as commonly used in the rubber industry, but like Thiotax, it has a somewhat bitter taste, so that this limits its use in rubber compounds which may come into contact with foodstuffs. *Thiofide* is entirely non-staining and as the odour which it imparts to compounds containing it, is not nearly so pronounced as is the case with Thiotax, this accelerator may be used very satisfactorily for applications where Thiotax is unsuitable.

Thiofide is an accelerator which may be combined with essentially all ordinary pigments and fillers. The normal small quantity of zinc oxide is necessary for activation purposes, but in contrast to Thiotax, large amounts of stearic or other fatty acid are not required. In gum stocks about $\frac{1}{2}$ to 1% of stearic acid is ample to give full activation, but in stocks containing carbon black, it is desirable to increase this to 2%.

This reduction in stearic acid content compared with what is necessary with Thiotax, lessens considerably any risk of blooming troubles being encountered. The addition of larger quantities than the above merely serves to delay the initial cures, and it is felt that with this accelerator increased handling safety is unnecessary.

Thiofide is generally used in production for cures ranging about as follows:—

45 mins. to 90 mins. at 30-lbs. steam.

30 „ 60 „ „ 40-lbs. „

10 „ 30 „ „ 60-lbs. „

8 „ 15 „ „ 80-lbs. „

It will immediately be realised that it is not a low temperature accelerator, and, in fact, is normally used at temperatures corresponding to 40-lbs. steam pressure and upwards.

The ageing properties obtainable at these higher temperatures are excellent. Thiofide stocks exhibit a very flat curing curve and so small differences in cure are minimised to a very large degree.

For manufacture where water cooling conditions are not of the best and where it is necessary to use an accelerator which will cause no processing difficulties, such as for extruding work at relatively high temperatures, Thiofide will be found to be of very great value.

It may be used in contrast to Thiotax under these trying conditions owing to its resistance to high temperature. This means that stocks containing Thiofide will not cure at say 220°F for a very long period of time indeed (such period we have found to be well over two hours). This accelerator, therefore, exhibits about the widest margin of safety of practically any accelerator

used to any extent at the present time. On account of this, Thiofide may well be termed a "fool-proof" accelerator in that scorching troubles during processing are practically non-existent and stocks may be stored in the factory without setting-up for a considerable period of time. In fact, we may abuse Thiofide stocks to an extent which, if applied to rubber compounds containing the faster accelerators, would cause them to be semi-cured in a very short time.

This accelerator finds extensive use in all classes of cable work, and is chosen chiefly on account of its ease of handling as described above. In cable work, it is also very essential that the rubber be uniformly cured and shall age well. Thiofide meets all these requirements and any irregularities which may occur owing to bad heat penetration are reasonably well smoothed out by this accelerator. The common accelerators D. P. G. and D. O. T. G. have also been used in this class of work, giving a fair degree of satisfaction, but the drawback to the use of these two accelerators is their well-known poor resistance to ageing. Their substitution by *Thiofide* will show a very marked improvement in the finished cable. This accelerator gives a low modulus in gum stocks, which is desirable for certain classes of work. For other types, higher modulus is required, and may be obtained by using A-32 or *Thiofide* in combination with other accelerators.

Thiofide finds ready application in all types of heavily compounded work such as flooring, and certain types of extruded hose. Wherever high temperatures are developed, on the mixing mill or on the extruder, it may be used with perfect safety.

In relatively pure gum stocks we generally use about 0.75 to 1% of *Thiofide* with about 2.75 to 3%.

of sulphur. For heavily compounded work, using the more absorptive pigments such as clay, etc., the accelerator content should be increased to about 1.25, whilst for tread stocks, about 1.1 or 1.2% *Thiofide* is common practice, again using 3% sulphur. Thus, another similarity between Thiotax and *Thiofide* is noted, in that both these accelerators are not absorbed to quite the same extent as are others commonly used. An interesting point is that it takes more sulphur than is becoming common now-a-days. For this reason it is inadvisable to try to compound for heat resistance using *Thiofide* as the accelerator. It has been found to be far more satisfactory to use an accelerator of the nature of Ureka in fairly high concentration and with about 16 parts of sulphur to 100 parts of rubber. By this method we can approach the ageing properties of a stock cured without free sulphur and yet not suffer from the tendency to reversion which is so often characteristic of this special type of compounding.

A study of the laboratory results will show that at low temperatures *Thiofide* stocks do not cure at all. This means that for moulding work, during the first few minutes of cure, the stock is quite soft and will flow easily. This is very desirable for obtaining the maximum adhesion between metal and rubber. Under the high pressure exerted by the press, the soft stock gets forced into the pores of the metal and then becomes cured. Thus, in reality the rubber is held by a myriad of cured veins of stock extending into the metal. Care should be taken to see that the stearic acid content is the minimum possible, on account of the danger of this blooming and spoiling the adhesion.

With regard to the question of using two accelerators, many believe that this provides a

better means of curing rubber than does the use of only one. The haphazard mixing of accelerators very seldom results in any tangible improvement. It is widely known that one can obtain very quick cures, comparable with those given by real ultra-accelerators, by using 50/50 mixtures of Thiotax and DPG. This combination is, however, so intensely scorchy, that there are very few factories which can handle the material satisfactorily.

Thiofide is a very much less active material than Thiotax at low temperatures. For this reason, attempts have been made to use small quantities of D. P. G. in conjunction with Thiofide. The resultant mixture gives a reasonably active accelerator, but it has essentially no delayed action in the generally accepted sense of the word. Consequently, special types of delayed action accelerators, such as Ureka and Ureka White, have been developed to give safety to the compound, with reasonably fast speed of cure.

Monsanto have grouped *Thiuram DS*, *Ultra Zinc DMC*, *Ultra DMC* together, since they are all products derived from dimethylamine and all provide acceleration of the ultra type.

Chemically, *Thiuram DS* is tetramethyl-thiuram disulphide. *Ultra DMC* is dimethyl-ammonium dimethyldithiocarbamate. *Ultra Zinc DMC* is the zinc salt of the previous acid, or zinc dimethyldithiocarbamate.

Thiuram DS is a faintly yellowish white powder with a melting point of 154°C when pure. The commercial material is similar in colour and melts at about 140°C . It is readily soluble in benzol, carbon bisulphide,

the chlorinated solvents and acetone, but only slightly so in petrol, cold alcohol and water. It is entirely non-toxic as commonly used in the Rubber Industry.

Thiuram DS has two distinct fields of application:—

1. As a combined accelerator and vulcanizing agent—that is to say, *without added sulphur*.
2. When used either alone, or in combination with another accelerator, in the ordinary type of rubber mixing, containing normal sulphur, to give very much quicker cures at ordinary or lower temperatures.

Practically all rubber manufacturers agree that the less combined sulphur one has in a stock, the better will be the ageing and heat resistant properties of that stock. Thiuram DS provides this sulphur in a highly active form by decomposition at the curing temperature, and very much less of this active sulphur is required for vulcanization than if we simply added sulphur to the mix in the ordinary way. By this means, we obtain really phenomenal ageing results together with very little tendency to reversion, and so, by proper compounding in this manner, we may obtain a very satisfactory heat resisting stock.

This use of Thiuram DS is, of course, only of interest in a specialized field, as it is a relatively expensive method of vulcanizing rubber. For the production of goods where the very best ageing results are the prime consideration, the use of Thiuram DS in this way will be amply repaid. Thiuram DS may be used similarly in the manufacture of insulated copper wire, as by this means of vulcanisation, essentially no tarnishing results during the cure.

When using Thiuram DS with no added sulphur, we normally use from 3 to 4% on the rubber, the higher amount being required for gas black or clay stocks, which materials retard the action of this accelerator somewhat. We can obtain a good technical cure at almost any steam pressure by adjusting the time. Thus, we may cure a stock containing 3% Thiuram DS equally well in 50 minutes at 20-lbs. as in 7 minutes at 60-lbs. steam pressure.

Although with reasonable care, no scorching troubles should be encountered, we would like to point out that scorching tendencies may be considerably reduced by the addition of $\frac{1}{2}$ to 1% Thiotax or Thiofide, without materially altering the rate of cure.

From 3 to 5% zinc oxide is necessary for complete activation, whilst for transparent goods, $\frac{1}{2}$ to 1% of the colloidal variety is sufficient. Stearic acid is not required for the proper functioning of Thiuram DS, although most compounders prefer to add up to 1% to smooth out any variations in the raw rubber.

In giving examples of the use of Thiuram DS as a vulcanizing agent, we wish to illustrate the general type of compounds in which it may be used with advantage.

The following stock shows in a remarkable degree the benefits which accrue to this type of vulcanisation, and is of special interest for the compounding of highly heat resistant inner tubes for use in the large size truck and passenger tyres:—

M-19			A	B
Smoked Sheets		100	100
Zinc Oxide		5	5
Soft Carbon Black			40	40
Stearic Acid		1	1
Sulphur		—	2
Thiuram DS		3	—
Thiotax	...		—	2
Flectol-B		1	1

Cure	Stock No.		Modulus at 300 %	Modulus at 500 %	Tensile at Break.	Ult. Elong.
25/40	M-19	A	623	1900	3920	680
		B	733	2160	4135	670
35/40	M-19	A	583	1885	4100	690
		B	772	2170	4275	675

These two cures were then aged at 121° C. with 100 lbs. air pressure. The corresponding figures are:—

Cure	Stock No.		Modulus at 300 %	Modulus at 500 %	Tensile at Break.	Ult. Elong
25/40	M-19	A	600	1965	3145	625
		B	1083	—	2415	490
35/40	M-19	A	578	1905	2980	615
		B	935	—	1870	410

Despite the very severe conditions to which these stocks have been subjected, the Thiuram DS cured stock, without added sulphur, has only perished about half as much as the normal cured Thiotax stock, and even this has less sulphur than is usual at the present time. The very great advantage of Thiuram DS in this type of work is at once obvious.

Thiuram DS may be used very satisfactorily in all types of moulded goods where quick cures are desirable. It is particularly useful for white and coloured articles.

When used in this way, Thiuram DS is usually faster curing than most of the Thiazole combinations, and is particularly more so than Thiotax or Thiofide, if used alone. However, the range of cure is not nearly as satisfactory as is obtained with the Thiazole type accelerators. It follows that Thiuram DS should only be used for relatively thin and small articles where uniform temperature conditions exist and where the control of the time of cure is reasonably accurate.

Thiuram DS finds very useful application in all types of latex work where steam or hot air curing of the deposited film is carried out.

When used alone with normal sulphur, Thiuram DS gives a very high modulus stock. It may be used with all compounding ingredients. It should be noted that it may cause discoloration of antimony stocks; also, that colloidal clays and carbon black retard its action. White substitute behaves similarly. Generally, such retardation may be overcome by increasing the Thiuram DS content. However, in the case of white substitute, the acid set free during cure must be neutralised by some basic material. In this respect we do not advise the use of magnesia, as although this is commonly used for this purpose with other accelerators, magnesia, together with lime, gives a very poor vulcanisate. An organic basic material such as triethanolamine is preferable.

The addition of Thiofide produces very peculiar results in that by adding more accelerator in the form of Thiofide, we get a decreased scorching tendency, less

risk of overcure and very little change in the rate of cure. We would like to point out in this connection that the addition of small quantities of Thiotax on the other hand, acts in a contrary manner by increasing the scorching tendency and produces a very high modulus stock.

The ageing properties of stocks cured with Thiuram DS alone without added anti-oxidant are reasonably good, although they are not as good as are obtained by the use of Ureka, Thiazole or Aldehyde accelerators.

The peaked curing curve and tendency to reversion exhibited by this accelerator may be avoided by using Thiuram DS in conjunction with another accelerator.

Thiuram DS is generally recognised as being one of the best accelerators for producing brightly coloured articles, as owing to the reduced temperature of curing, the colour is correspondingly less affected during cure and much less fading results.

Thiuram DS used with another Accelerator.

"*Thiuram DS*" may be used with excellent results in conjunction with some slower accelerator. Thiotax and Thiofide alone give relatively low modulus stocks with medium tensiles but good ageing properties. Frequently it is desirable to produce a stiffer stock and at the same time, avoid having to change over to another type of accelerator. This is one of the occasions where Thiuram DS may be advantageously employed.

For example, a gum stock containing 3% sulphur and 1% Thiotax gives a stock with a modulus at 500% elongation of between 200 and 500 lbs. per square inch with a tensile of perhaps 3,600 lbs. depending on the cure. By adding 0.1% Thiuram DS to this compound,

the resulting stock shows a corresponding modulus of about 1,000 with a break figure of 4,500-lbs. together with a slightly faster cure. The combination is still easily workable under ordinary factory conditions.

Generally speaking, the addition of 0.1 to 0.2% of Thiuram DS to any Thiotax or Thiofide stock will materially enhance the strength and give increased heat resistance, at the same time, speeding up the cure appreciably. This type of combination becomes very useful in repair work and for general moulded articles giving splendid results.

Thus we are enabled to take advantage of the good age resistant properties and general plateau effect of the Thiofide or Thiotax, and yet speed up the cure, which enables us to make fuller use of the mould equipment at our disposal. By adjusting the proportions, one may obtain almost any degree of activity with relative freedom from scorching. It must be borne in mind that the more active combinations are naturally more prone to scorch during processing, and suitable care should be taken.

“Ultra DMC” is a white powder soluble in water, alcohol, and hot benzene. The stability of this accelerator, however, is unsatisfactory in that it decomposes slowly at room temperature and more rapidly as the temperature is raised. With this decomposition, we get a gradual falling off in curing power and so this accelerator is not to be recommended unless regular fresh supplies can be obtained from the manufacturer and even then, these must be used up in production almost immediately. This is highly unsatisfactory from the factory point of view.

The Zinc salt of this acid derived from Ultra DMC or Ultra Zinc DMC, however, is perfectly stable at all temperatures and gives essentially the same vulcanising characteristics. Thus the use of Ultra DMC is comparatively negligible since nearly every manufacturer prefers to use the Zinc salt.

The following figures show the equivalence of the two accelerators when employed in equi-molecular proportions in a gum stock.

M-19			C			D	
	Rubber	100		100	
	Zinc Oxide	5		5	
	Stearic Acid	0.5		0.5	
	Sulphur	2		2	
	Ultra Zinc DMC	0.25		—	
	Ultra DMC	—		0.28	

Cure	Stock		Modulus at			Tensile at Break.	Ult. Elong.
			300%	500%	700%		
15/10	M-19	C	194	486	1725	3060	805
		D	190	475	1740	2965	800
20/10	M-19	C	221	592	2140	3525	790
		D	209	583	2185	3610	795
30/10	M-19	C	242	644	2465	3465	760
		D	261	712	2600	3695	765
45/10	M-19	C	243	616	2275	3640	785
		D	281	775	2915	3620	735

One further point is that Ultra Zinc DCM exhibits the wider margin of safety at low temperatures as is shown by the fact that the above stock D begins to scorch after 60 minutes at 80°C, whilst stock C does

not start to set up until 120 minutes at this temperature. Future discussion will, therefore, be confined to the use of Ultra Zinc DMC.

“Ultra Zinc DMC” is a true ultra-accelerator and used alone will vulcanise stocks on standing at room temperatures. This prohibits its use in the ordinary way of handling rubber stocks. Either stocks containing it must be processed promptly and all waste used up promptly, or else it must only be used as a secondary accelerator in relatively small amounts.

Used alone, however, Ultra Zinc DMC is admirably suited for latex work. It disperses very nicely with normal compounded latex. The latex may cure a little on standing but the viscosity remains essentially unaltered so that the slight vulcanisation that does take place is not of great consequence. Later, complete vulcanisation may be carried out at temperatures as low as 50° to 70° C, although generally a higher air temperature is used, or the article is vulcanised by dipping in boiling water.

Similarly, Ultra Zinc DMC is an excellent accelerator for the making up of self-curing rubber cements.

Used as a secondary accelerator, Ultra Zinc DMC has real advantages. Where processing is good and where we are able to handle a slightly faster curing stock than is given by the use of Ureka or Ureka White alone, the addition of fractions of 1% of Ultra Zinc DMC will speed up the rate of cure to any reasonable degree of activity.

Furthermore, to get greater reinforcement from Thiotax or Thiofide stocks, we may either add a basic material such as DPG which gives us the required

stiffness, but also produces a very scorchy combination; or, we may use Ultra Zinc DMC in very small amounts which does the reinforcing without giving us too touchy a mixture.

The amount of this accelerator to be used in this way depends on the result required. In this respect it is well to remember that more can be added with the same degree of safety to Thiofide stocks than to the corresponding Thiotax ones. As a general rule, 0.2% is added to the former and 0.1% to the latter.

Similarly Ultra Zinc DMC may be added to a Thiotax tread stock giving remarkably increased abrasion resistance. This combination is, however, generally considered too scorchy for most factories to handle. A similar result is obtained by treating a Thiofide stock in the same way, but here we have a wider margin of safety for handling purposes.

This reinforcing action of Ultra Zinc DMC, added in small quantities, is not confined merely to black stocks. With all rubber mixes reinforced either by zinc oxide, magnesium carbonate, whiting, etc., one gets a notable increase in the stiffness and this is just what is wanted in certain cases. This action is particularly noticeable in the case of zinc oxide stocks using Thiofide as the primary accelerator, where, by adding as little as 0.1% Ultra Zinc DMC, the modulus is trebled whilst the scorching tendency is negligibly increased.

Warning!

We would like to warn the users of the three accelerators just described, that the careless use of any one of them will only cause a lot of processing troubles. The best results are only obtained by the use of a really

balanced formula together with suitable care in handling. And, in respect to the use of these particular accelerators we would emphasize the necessity for stocks containing them to be thoroughly cooled by air or water dipping, when coming from the mixing mills, calenders or extruding machine and before being stored away or rolled up for the making up rooms. This is particularly imperative in hot climate where the stocks take a correspondingly longer time to cool down. Scrap from the making up rooms also should be worked away as soon as it becomes available and not permitted to lie around the mill room for longer than necessary.

If these simple precautions are taken, we feel that excellent results may be obtained by the use of these accelerators, the many uses of which we have just attempted to describe.

The Imperial Chemical Industries Products have already been discussed in Volume I, and in Chapters IX and X of this Volume, several formulas are given embodying the I. C. I. chemicals, which the author has worked for some time and found very satisfactory.

The following are further I. C. I. accelerators, the use of which can be recommended. Their water-soluble accelerators can be easily introduced into rubber latex mixings in the form of aqueous solution of any desired strength. These are:—

Vulcafor SPX, which is a sodium isopropyl xanthate combination,

Vulcafor DDC, which is diethylammonium diethyldithiocarbamate, and

Vulcafor SDC, which is a sodium diethyldithiocarbamate combination.

I. C. I. state that these three types are very active accelerators which, when combined with sulphur and zinc oxide, will bring about the vulcanisation of rubber in the course of a few days at room temperatures. They recommend the use of from $\frac{1}{2}$ to 1 part of accelerator (dry weight), about $1\frac{1}{2}$ to 2 parts of colloidal sulphur, and at least 1 part of colloidal zinc oxide, all calculated on 100 parts of dry rubber contained in the mix. These quantities, they say, may be varied within limits depending upon the type of rubber compound and the conditions of vulcanisation it is proposed to employ. For example, for dipped goods, a mix containing 1.5% of colloidal sulphur, 1% of colloidal zinc oxide and 0.5% of Vulcafor SDC, all calculated "dry weight" on 100 parts of dry rubber, will cure in about 20 minutes at 190° F. to 200° F. in hot air, or in a few days at ordinary room temperature.

Water-soluble accelerators can also be used for curing thin rubber articles such as gloves or balloons by immersing the mould in a hot aqueous solution of the accelerator. Thus a film of rubber containing 1.5% of colloidal sulphur and 1% of colloidal zinc oxide may be vulcanised by immersion for about 20 minutes in a bath containing a 1% solution of Vulcafor SDC at about 200° F.

We are giving further the comments of the Imperial Chemical Industries on their Ultra and Super-accelerators.

They state, that in the list of Ultra Accelerators, can be included a series of accelerators which are mainly the salts of Xanthic or Carbamic Acid. It is surprising to know that with the introduction of Ultra-Accelerators, mixes have been obtained where small additions of these accelerators have given excellent vulcanisates.

As against the other type of accelerators, vulcanisation can be carried out at very low temperatures, and in certain cases even at room temperatures within 48 hours.

Vulcafor ZIX — (zinc isopropylxanthate) — is a white powder with a sharp smell, has a melting point of 145°C ., is active at room temperature, and its main application is in self-curing cements. It cannot be used efficiently at temperatures above 100°C ., because of decomposition.

When ZIX is used, it is necessary to adopt the two-batch method, i. e. to make up a mix in two portions, one containing the sulphur, and the other the accelerator. Two parts of ZIX and four parts of sulphur, with each 100 parts of rubber, should be used in the mix. Zinc oxide is necessary as an activator.

During the mixing process the work is to be carried out at as low a temperature as possible.

Ultra-accelerators are now-a-days indispensable on account of their quick-curing property. Compounds with these accelerators, provided they have a low sulphur content, give greater transparency and brilliancy to the vulcanised product, specially when crepe rubber is used, the reduction of the sulphur content imparting also better ageing properties, even without the addition of anti-oxidants.

Though, in the beginning, some difficulty is experienced in manipulating mixes made with ultra-accelerators, due to their extraordinary activity, such difficulty can easily be obviated with care and experience.

For latex work, ZIX, which is insoluble in water, should be dispersed in the ball mill with a dispersing agent like the I. C. I. Dispersol L, and then incorporated in the latex mix, the sulphur being added at the last moment, just before use.

Vulcafor P is a pale cream powder with a faint characteristic smell of Piperidine Salt.

The product is soluble in most of the usual solvents and has good solubility in rubber.

The pure product has a melting point at 169° C.

In its curing properties Vulcafor P is as good as ZDC or SDC, but has a few advantages over them.

With zinc oxide, this accelerator is one of the most active accelerators.

High class, pale transparent goods can be produced by using Vulcafor P.

Vulcafor P is quite suitable for Latex work, giving vulcanisates of high tensile strength. It is generally used in quantities up to 1% on the weight of rubber in Latex, and should be activated with zinc oxide.

When using Vulcafor P, care should be taken not to store the material too long as the mixes will vulcanise at room temperature in about eight days. Vulcafor P is specially suited for obtaining completely transparent films with latex mixes. The procedure for making such transparent films is as follows:—

Dried films prepared from uncompounded latex are dipped for 10 seconds in a solution of

Benzene	100	parts
Vulcafor P	3	,,
Sulphur	2	,,
Zinc Oxide	1	,,

and dried completely. Cure at 100°C from 30 to 40 minutes gives the required effect.

Vulcafor DHC is a soft cream coloured powder with a faint odour. The product is completely soluble in Benzene and melts at 148°C.

In latex mixes Vulcafor DHC is non-staining and gives brilliant results.

There is practically no other accelerator than Vulcafor DHC which can give better transparent results.

Vulcafor ZDC (zinc diethyldithiocarbamate) is a white coloured powder, with a faint smell. It is insoluble in water and melts at 175°C.

Vulcafor ZDC is one of the most active accelerators which finds a varied use in the Latex Industry. Because of its zinc content, the product functions effectively without zinc oxide activator.

This has an advantage as very transparent films can only be obtained without the use of zinc oxide. However, small proportions of this product give quick-curing mixes.

Vulcafor SPX (sodium isopropylxanthate) is a pale yellow powder with a melting point of 124°C.

Vulcafor SPX has the same vulcanisation properties as Vulcafor ZIX, only that the former is water-soluble, while Vulcafor ZIX is insoluble in water. It is also used exactly in the same way as ZIX.

When used in conjunction with Vulcafor DDCN, it gives quick-curing mixes which vulcanise at room temperature.

As in the case of Vulcafor ZIX, SPX should be used in a two-batch mix, and should not be cured over 100°C.

Vulcafor DDCN is a pale yellow powder with characteristic smell. It melts at 75°C.

Vulcafor DDCN is a water-soluble accelerator and is much more active than Vulcafor ZDC. This is of advantage where quick-curing mixes are required.

Vulcafor DDCN can be used in conjunction with Vulcafor SPX and ZIX in mixes which should cure at room temperature, but cure over 141°C. is not recommended.

Vulcafor SDC (sodium diethyldithiocarbamate) is a pale yellow powder with a characteristic smell, and melts at 150°C.

Vulcafor SDC is not suitable for temperatures above 141°C (40 lbs.)

This Accelerator is quite as active as Vulcafor ZDC, but is used only when water-soluble form of ZDC is required.

It has no special advantage over ZDC.

Besides the above mentioned ultra-accelerators which are true salts of Carbamic or Xanthic Acid, there are many others which are quite different in constitution. Vulcafor **TMT** and **TET** are the most important of these. Both are equally active, except for the fact that Vulcafor TET is safer to use in mixes containing very little sulphur.

The Monsanto "*Santovar A*", which is an alkylated-polyhydroxyphenol product, is nearly a white crystalline powder with a specific gravity of 1.049, has a melting point not less than 165° C., and is completely soluble in twice its weight of acetone.

"Santovar A" was developed as a non-discolouring anti-oxidant for white stocks such as side walls, shoes etc. In addition to being an anti-oxidant, it affords excellent protection against sun checking. In uncured compounds, "Santovar A" inhibits the deleterious action of sunlight. This unique property is used to advantage in such articles as crepe soles, uncured rubber films, etc.

Further, the persistent action of most chemical plasticizers is stopped by "Santovar A" and the addition of a small amount of that product to re-milled scrap containing a plasticizer prevents the stock from becoming unduly soft.

The Monsanto "*Santoflex B*" is the reaction product of acetone and para amino diphenyl. It is a waxy dark grey lumpy solid with a crystallizing point at about 80° C. and has a specific gravity of 1.045.

"Santoflex B" was developed as an anti-oxidant for tyres and tubes, but its exceptional properties led also to its adoption in many other classes of rubber goods. Because of its excellent effect on ageing and flexing, "Santoflex B" is used today as a general purpose anti-oxidant. It is compounded successfully into such items as tyres, tubes, hoses, heels, soles, beltings, etc.

"Santoflex B" being a solid, is easy to handle and yet disperses readily on the mill, but it activates acceleration very slightly, when combined with Captax or its derivatives.

The Monsanto "*Santoflex BX*" is a constant composition blend of "Santoflex B" and diphenyl-para-phenylene-diamine. It is also a waxy, dark grey, lumpy solid, having a specific gravity of 1.11.

"Santoflex BX" has all the excellent properties of Santoflex B plus diphenyl-para-phenylene-diamine, the latter material being able to improve the flexing life of many rubber compounds, particularly those of the tread type. The diphenyl material noticeably activates the cure of MBT and MBT-derivative-accelerators, but it discolours light stocks very badly.

CHAPTER IV.

Chemicals.

DETAILS regarding chemicals used as fillers in rubber compounds were given in Chapter VI, Vol. I; and though the use of Carbon Blacks in the rubber manufacturing process was fully explained, the matter is so complex that it would need further explanation.

There are several types of Blacks, the most important being the Channel Process Carbon Black, which is definitely an *Active Black*, usually known as *Gas Black*. Within the range of Channel Blacks—the word ‘Channel’ being used because of the method of manufacturing this quality of Black—there are soft, medium and hard types, or better still, soft particle, medium particle and coarse particle types of blacks.

Furnace Blacks are *Soft Blacks* comprising the Castex and the P-33 types. All these are semi-reinforced blacks produced by a modification of the manufacturing conditions from the same source as Channel Blacks.

Thermatomic Blacks are slightly less reinforcing than Furnace Blacks and include the Thermax type and the like.

Lamp Blacks or *Oil Blacks* come under the category of *Inactive Blacks*.

In short there are *Eight Varieties of Carbon Blacks*, to be taken into consideration in the manufacture of rubber:—

Dixie Gas Carbon Black. Soft black—gives excellent tensile and modulus properties—suitable for tyre compounding.

Thermax Carbon Black. Soft thermatomic carbon—can replace many mineral fillers with production of greater resilience, better strength and tear resistance, and equally good ageing quality—low volume cost—dark grey in colour—soft black—most useful in the production of inexpensive articles as well as high grade mechanical goods of all kinds.

Micronex Beads are active and dustless.

Fumonex or Castex. Softer than Micronex—gives high resilience, easier mixing and extrusion properties,—for rubber hoses and the like.

Velvetex. Contains a tarry softener—used for the production of soft tyre frictions.

Gas Black P-33, is an inactive Gas Black.

Carbon Black Arrow is an active black of the Micronex type.

Channel Blacks are noted for their stiffening and deadening effect, they are jet black in colour.

*The Glyco Chemicals Co.** have recently issued an interesting nomenclature of chemicals they are

Glyco Product Co., 26 Court Street, Brooklyn, New York.

able to supply to the Rubber Industry, but due to war restrictions and various difficulties in obtaining the right product, they have meantime given more substitutes, which can easily serve the purpose. Furthermore, as this Volume contains a part devoted to Synthetic Rubber, we also give below the products suggested by the Glyco Chemicals which may be of interest to that Industry.

The various synthetic rubbers—they say—now being manufactured have introduced many new complications. Because they are different organically from natural rubber, many variations in formulation and technique are necessary to produce satisfactory finished products, while the chief problem has been the lack of a good, economical and readily available plasticizer.

So they have, recently introduced a plasticizer for synthetic rubber which is both economical and effective in use. This plasticizer is known as Plasticizer S-125 and is being used to replace Dibutyl-Phthalate and similar plasticizers, very efficiently, at a lower cost per pound of finished product. When used in amounts of 5% to 10%, Plasticizer S-125 gives a flexibility to the cured stock equally as good as 20% to 30% Dibutyl-Phthalate, and does not exude from the stock. Furthermore, in these amounts, Plasticizer S-125 has definite lubricating tendencies, thus facilitating release from the moulds.

This plasticizer, being insoluble in mineral and vegetable oils, gives added resistance to greases and oils when the synthetic rubber is used for hoses, gaskets, packings, etc. Its low freezing point is of interest for low temperature work. It has a definite wetting tendency for pigments, thus enabling them

to be milled in to the stock, giving easier and quicker grinding as well as more uniform dispersion throughout the stock. In adding Plasticizer S-125 to the synthetic rubber, it is advisable to add slowly in small portions, allowing each portion to be digested by the stock on the mill before the next portion is added. This eliminates any possibility of slip on the mill.

As *Carnauba Wax*, which is used sometimes in insulation mixes and for polishing ebonite articles, is not always available, it can be satisfactorily replaced by *Albacer*. The best solvent for Albacer is a mixture of one part ethylene dichloride, six parts of toluol and four parts of butyl acetate. This mixture will dissolve up to 5% Albacer, most of which will remain in solution even at room temperature.

Albacer is a white hard wax with a high lustre, having a melting point of 95 to 97° C., is insoluble in water and completely soluble in hot hydrocarbons. Albacer can also be dissolved by heat in Turkelene—1 lb. Albacer in 2 qts. of Turkelene,—this gives a non-greasy high polish on ebonite articles. Turkelene is an emulsifying agent which replaces sulphonated oils in many instances—about 3 to 4 oz. are required in what the Glyco Chemicals call the “Standard 1½ bushel tumbling barrel”. The ebonite is tumbled for about 16 hours either in sawdust or wooden pegs, which are slightly wet with the polishing solvents.

Where a volatile solvent is desired, Albacer may be dissolved by heat in approximately 1 gallon of naphtha, or a high boiling solvent such as Varnolene, and if a pint of Butanol is added to the solvent, more of the wax will remain dissolved at room temperature. Further, wax which separates in fine particles should

be re-dispersed by stirring before adding the proper quantity to the tumbling barrel.

The Glyco Products suggest their *Ammonium Stearate (Paste) S* to be incorporated in the rubber cements as an adhesive agent of the rubber to the cloth on vulcanisation. It increases the coverage and gives smoother compounds. 4% of Ammonium Stearate (Paste) S should be used calculated on the rubber content in the mix.

Ammonium Stearate (Paste) S is a pearly white soft paste with an ammoniacal odour, is soluble in water and alcohol, emulsifies the hydrocarbons, has a pH value (5% aqueous dispersion at 25° C.) of 9.5 to 9.7, and a specific gravity of 0.96.

The Glyco "*Diglycole Stearate S*" is a protective coating agent and from $\frac{1}{2}$ to 2% as a dispersion in water, is used to prevent tacking of raw rubber sheets at the plantations. The dispersion may be applied either by spraying or by dipping and will not affect the future working of the rubber.

The Glyco "*Glaurin*", which is Diethylene Glycol Mono Laurate is a plasticizer and softener, can be introduced in rubber compounds in small quantities, to be determined after tests, and gives excellent results.

A new "full dress" finish for rubber, synthetics and rubberised fabrics, when high elasticity is required, is the Glyco "*Hevealac*" which is a resin solution (in alcohol). It dries rapidly, gives a high gloss and can be applied by brushing, dipping, or spraying. Coatings

with Hevealac are clear and bright and can be used for all practical purposes, they are non-inflammable when dry, adhere strongly to most surfaces and retain the flexibility of the product at low temperatures. Hevealac is unaffected by water, oils and most hydrocarbons.

For latex composition, the Glyco Chemicals suggest their "**Foamex**". It is a foam retarder which can be used in water solutions of glue or casein for the latex industry. In general, as little as one ounce of Foamex to 10 gallons of solution is sufficient for most purposes, and in this proportion the product will not interfere with the other properties of latex.

Foamex is a pale yellow liquid with no odour, having a specific gravity of 0.96 to 0.97.

The Glyco Deodorizing agents are the "Lemenone" (a thin white oil, having a lemon-lime odour, the "Clovel" (a yellow oil having a clove odour), and the "Coverene" (a light coloured liquid with a pleasant odour). Coverene is insoluble in water, but completely soluble in oils, hydrocarbon solvents and the like. Coverene is being used in America very successfully for re-odorizing and deodorizing raw rubber and latex. Its use as a rubber deodorant is recommended in proportions of $\frac{1}{2}$ % to 1 % based on the total weight of the rubber mix. Further, Coverene does not affect the properties of the rubber and gives a lasting but pleasant odour to the finished product.

The Imperial Chemical Industries have produced a Rubber Mastication Paste which they call their *Rubber Mastication Paste I. C. I.*

It is a special combination of fatty acids, oils and an anti-oxidant. The product is specially suited and manufactured for aiding the mastication of rubber stocks. This paste affords a uniform mastication and gives vulcanisates with a soft feel. In heavy loaded goods, the addition of oils required for masticating and softening the stocks gives very sticky results. When replaced by Mastication Paste, I. C. I. the results have a firmer handle and show better ageing properties. Some articles have to be specially manufactured which show improved ageing against sun-light and air. Though it is not claimed that Rubber Mastication Paste I. C. I. is designed to completely offer a remedy against such effects, the results obtained by incorporating the paste are very encouraging.

In the tyre and tread industry Vulcafor MBT is usually the main accelerator and, as already known, stocks containing MBT require the addition of Stearic Acid. Rubber Mastication Paste I. C. I. used in conjunction with Vulcaflex A, under these conditions, helps to reduce the quantity of Stearic acid. The articles so prepared have a greater resistance against flex and heat.

General proportion of this paste is from 2 to 4 %.

Rubber Mastication Paste I. C. I. has also been able to replace the oil emulsions in dipped goods. A convenient proportion to be employed is 0.2 to 0.4 parts for every 100 parts of dry rubber content in latex. Very good dispersions are obtained by the addition of Dispersol L Paste in the usual way.

CHAPTER V.

Raw Rubber- Chlorinated Rubber- Reclaimed Rubber.

Raw Rubber.

THERE is a world-wide scarcity for raw rubber at the present time. This is due mainly to Japanese occupation of Malaya States and the East Indies, two of the main sources of raw rubber supply, and attempts have been made to discover other sources which could replace the lost supply of rubber.

There are thousands of species of trees, shrubs, vines, and small herbaceous plants that contain rubber. They grow all over the world; especially in tropical regions, and it is likely that India may have a good number of them. A conscientious survey would surely reveal much.

The "*Cryptostegia*" is a plant which was recently discovered in India, in the Tinnevely District, and the following is a statement made by the Special Assistant, Wild Rubber Scheme, Madras Province, regarding this newly discovered plant:—

"The usual bark tapping method, that is employed in the case of Hevea, cannot be employed for *Cryptostegia* plants owing to the small girth of the trunk, its irregular shape and the corrugations appearing in it. The satisfactory method for extracting the rubber, which has been so far practised is to clip off the ends of four or five shoots or tender twigs by means of pruning scissors or knives and thrust these into the mouth of a bamboo tube. Latex drips into the tube for a few minutes, and then the flow ceases. A button or plug of rubber is found at the end of each cut twig, which can be collected the next day. A clipper could handle 1000 shoots in a working day of 7 hours. Plugs or buttons form a very important source of rubber. Coagulation of the latex is effected by ordinary water. When latex is diluted with 9 parts of hot water, coagulation is effected in about an hour. The water is mixed in the proportion of 2 parts of boiling water to 7 parts of cold water. Rubber Technologists have certified that *cryptostegia* rubber could be utilised even for high grade mechanical rubber".

The June 1942 issue of "India Rubber World" gives a quite different aspect of the said plant. It states that *Cryptostegia* has its origin in Madagascar and is found in abundance in Africa.

It is further explained that the two species of Madagascar rubber vines, — "*Cryptostegia Grandiflora*" and "*Cryptostegia Madagascariensis*" — are being planted in many parts of Florida, and because of their foliage and flowers are used for ornamental purposes. The first plant is a large climber, while the second takes the form of a broad round bush five or six feet high. A hybrid of the species also has been propagated and studied in Florida.

Rubber obtained from "Cryptostegia" has been tested and found to be of good quality, but the present supplies are limited. The percentage of rubber in the roots, stem and leaves is very low, running only 2% to 3%, and the cost of extraction of the rubber is high. Extraction of rubber from ornamental plants in Florida might yield small quantities of rubber, but for the immediate emergency propagation or reproduction would be very slow and no appreciable quantities could be expected from this source within the next several years. "Cryptostegia" is a plant which could be handled by machinery devised for extracting rubber from guayule*, but, because of the low rubber content, the extraction will be costly. Considering the low yield, the time required for large production, the difficulties of extraction, and the low percentage of rubber, Cryptostegia is not regarded, in America, as a practical source of rubber supply, during an emergency comparable to the present.

"*Milkweeds*" is another species of rubber-yielding plants, according to the "India Rubber World" and experiments were carried out with these native rubber—yielding plants of the hot desert districts of Southern California and Arizona, where a promising species called the "*Asclepias Subulate*" was discovered. This is a plant with tapering, slender stems, growing in clumps like a large bunch of grass. Another desert milkweed, which has been tested and found to contain a higher quantity of rubber than *Asclepias Subulate*, is "*Asclepias Eroas*". Methods of cultivating these plants have been worked out, and it has been demonstrated that they could be grown in large quantities in the desert districts. But in cultivation tests, so

far, the yield of rubber from these plants has been so low that it has never been possible to obtain more than 80 to 90 lbs. of rubber per acre per year, from either of these species.

The common broad-leaf milkweed called "*Asclepias Aspira*" found in the eastern parts of the U. S. A., then attracted attention, but this plant has proved less promising than either of the two milkweeds mentioned above.

In fact, it is said that no member of the milkweed family could be considered to equal the American Guayule.

The "*Euphorbias*" group contains innumerable species of rubber-yielding plants closely related to the "Hevea" tree, writes the "India Rubber World". However, only one of this group has ever been an important source of crude rubber. It is the "*Euphorbias Intisy*", native to Madagascar, but cultivation experiments with this plant, in the United States, have been disappointing, as it has been impossible to obtain seeds, whereas reproduction by cuttings has been very slow. It takes a period of many years to grow the plant, and it will have to be destroyed to obtain the rubber.

The common Christmas plant "*Poinsettia*" is also a member of this group, and has been promoted and tested for rubber production. Reliable tests have demonstrated that the rubber content of this plant is too low for serious consideration.

Russian Rubber Plants. Several rubber productive plants have been discovered in that part of Asia under Russian rule, and many of them have been cultivated on a fairly large scale. The "*Kok-sagyz*",

which is a species of "Taraxacum" or dandelion, states the "India Rubber World" June 1942, is one of them. But current favourable reports on this plant do not appear to be verified by records of actual field performance in Russia, received from reliable sources. In contrast to the reported rubber content in the roots of 10 to 27%, recent information from Russia indicates only a maximum percentage rubber of 3 to 5% and an average of 1 to 1½%. From the same source, it also appears that the average yield of the "Kok-sagyz" root, per acre, is about half a ton. On the basis of maximum rubber content, this would be only 50 lbs. of rubber per acre, which is indeed very small.

Other plants tested by the Russians are the "*Tau-sagyz*"—which is a species of "Soorzonera" related to black salsify—and the "*Krim-sagyz*", which is also related to the dandelion group, but all the results obtained, in Russia, from the latter are less favourable than those from "Kok-sagyz".

The "*Goldenrod*", writes the "India Rubber World", in its June 1942 issue, is one of the several species, native to the United States, discovered by Mr. Thomas A. Edison, which he tested for rubber and found to be most promising in as far as rubber content was concerned. But the rubber obtained from this plant was hardly comparable to the para rubber. It had only 50% of tensile strength compared with compounds made of para rubber. Satisfactory methods for extraction of the rubber have so far not been devised, and the cost of the present method of extraction by chemical solvents is very high and inefficient. Only a small amount of propagated material of improved strains of "Goldenrod" is available at the present time, and the "India Rubber World"—June

1942—stated that a maximum planting of 60 acres in 1942 was possible, to be followed by a twenty-fold increase in 1943.

The "*Chrysanthamus*" or "*Rabbit Brush*" is another American rubber-yielding plant, the latex of which contains 6% of dry rubber. Results in survey publication of 1919, states "India Rubber World" June, 1942, indicate that appreciable quantities of rubber could be obtained from these wild plants, say from 30 to 40,000 tons, but at enormous expenditure of labour.

Osage-Orange is still another rubber-yielding plant, botanically known as "*Maclura pomifera*", but tests conducted in America have failed to show even 1% rubber in the fruits of the plant, and analysis of other parts of the plant have been equally disappointing.

"*Micro Organisms*". We learn from "India Rubber World"—June 1942—that the possibility of synthesis of rubber by the use of bacteria, or other micro-organisms, has been suggested in America. The idea is to inoculate expressed juice of rubber-bearing plants and increase the amount of rubber yield from a given weight of the plants.

As the rubber-bearing plant itself synthesizes rubber, there is no reason to doubt this possibility provided the necessary elements, or materials, are in the expressed juice, or in the air, and available to the micro-organisms. Successful use of such methods to produce rubber have not yet been demonstrated. In conclusion, of all the species of rubber-yielding trees, shrubs, vines, and small herbaceous plants, described by the "India Rubber World"—June

1942,—except for the hevea tree, it is the American “guayule” which seems to be the most promising.

Guayule is not a new-comer, because even thirty years ago, we used to produce rubber goods from it, in Belgium, and our experience was that guayule mixes were vulcanising more quickly, and at lower temperature, than any other sort of rubber then in use. It had an unpleasant odour. Even vulcanised motor car tubes, made from it, retained that disagreeable odour for a long time after manufacture.

II

Chlorinated Rubber.

Chlorinated Rubber is not a novelty. The idea of it was discovered long ago. What led to the discovery of this product is unknown to us. It may be presumed that scientists of early days tried to remove the tackiness from rubber by means of chlorine. It seems, however, that they were unsuccessful, whereas many years later Charles Goodyear, perhaps aware of the failure of the chlorine process, attempted to remove the tackiness by immersing the rubber in a bath of melted sulphur, and his trial was a complete success. The promoters of chlorinated rubber, however, did not lose heart but continued their experiments with chlorine, and though they did not produce elastic rubber, they discovered something which had its source from the rubber. By exposing the raw rubber dissolved in chloroform to the action of chlorine, they obtained a leather-like mass. Chemists then discovered that chlorine reacted with rubber and their analyses showed, that in the product they had obtained, six atoms of chlorine were

added and two atoms of chlorine were substituted, the product having the formula $(C_{10} H_{13} Cl_7)$.

Peachy, in Great Britain, developed the process further and after many trials, and investigations, patented the rubber heptachloride he had obtained by getting chlorine in excess into a chloroform solution of rubber. His product was marketed under the name of "*Duroprene*" and found its application in varnishes for acid and water proofing of leather and fabrics.

Chlorinated rubber then attracted the attention of Germans who produced solutions of less viscosity, by which they enlarged the field of application of the product. From all these experiments, it has become clear that the nature of chlorinated rubber is not stable, but that it varies, and depends upon the temperature used during the process of chlorination, the kind of solvent adopted, and the degree to which the raw rubber has been broken down. Today's commercial product is non-inflammable, and resists the action of petrol solvents and oxidising agents, but it is soluble in coal-tar-naphta. Its specific gravity is 0.086. It is a yellow powder and besides having other uses, finds its application in fire-resistant rubber mixes and in certain combinations with synthetic solutions, as may be seen from the chapter devoted to Synthetic Rubbers.

III

Reclaimed Rubber.

In Volume I, Chapter VII, we have described the theory regarding reclaimed rubber and stated that there are various types and grades of reclaim, the best and

the most widely used being the one obtained by the *Alkali Process*. Two other processes for reclaiming waste rubber are the *Acid Process* and the *Oil Process*.

By both the alkali and acid processes, the rubber-containing fabric is subjected first to the action of sodium hydroxide, and then treated with dilute sulphuric acid, with the purpose not only to reclaim the rubber waste, but to hydrolise* the fabric. The material is then allowed to remain in the vulcaniser for several hours under 200 lbs. steam pressure, after which it is washed thoroughly, not only to remove excess alkali or excess acid, but also to remove the hydrocellulose which has been formed as a result of the hydrolysis of the cotton fabric which is part of the waste.

A fourth process for reclaiming waste rubber has now been developed, which may be termed the "*Turmoil Process*", or better the "*Ignition Process*". This process is applicable to waste rubber with or without fabric.

Rubber waste without fabric was submitted to this process for two hours at 200° C. in an electrically heated vulcaniser. The waste was then removed, and appeared as a plastic mass which dissolved in solvent in a short period of time producing a solution absolutely sticky and very suitable for the fabrication of insulating tape. The trial was then applied to rubber waste containing fabric, the intention being to submit it in the electrical vulcaniser at a temperature of 400 to 500° C. Unfortunately, after having obtained a temperature of 250° C., the elements in the vulcaniser melted, and it

* *Hydrolysis* is the term employed for the interaction between a salt and water whereby free acid and free base, or an acid and a basic salt are formed. Hydrolysis is thus a kind of reversion of the process of neutralisation of an acid with a base, or of a base with an acid.

become necessary to suspend the experiment until such time as adequate elements become available, perhaps after the war. On examination of the waste, the rubber part was sticky as was the case with the first experiment, but the fabric was almost completely carbonised, so much so that our conclusion is that, provided the waste can be heated for 3 or 4 hours in the vulcaniser at $500^{\circ}\text{C}.$, there will remain only a few cinders of the fabric which, if they remain in the reclaim, can be easily amalgamated with it in the solvent, producing a sticky solution suitable for the fabrication of insulating tape.

Thus, by the "*Ignition Process*", one can reclaim rubber without the help of an alkali, or acid, or oil, and by working the process, after various trials, it should not be surprising to find that fillers and sulphur can be added to the rubber thus reclaimed.

Solution from Reclaim.

So far there has never been the question of producing rubber solution from reclaimed rubber. The I. C. I. have described a method which, after trials, has been found to be quite workable.

The following compound composed by them, is extremely sticky, and can be used for a number of purposes:—

Whole tyre reclaim	100	parts	by weight.
Wood Rosin	75	"	"
Lined Rosin	25	"	"
Solvent	300	"	"

The dry ingredients are mixed on a roller mill and the compound is then let down in the solvent, which may consist of petroleum spirit, or solvent-naphtha, or a non-inflammable solvent such as tri-chlorethylene.

The above compound is limited in its application by the fact that it remains permanently sticky and is thermoplastic.

Self-curing rubber cements, based on reclaimed rubber, have been developed, but are more suitable for certain purposes, such as for joining fabrics. The following two adhesives will serve as examples, the quantities indicated being parts by weight.

Compound	Adhesive I.		Adhesive II.	
	A.	B.	A.	B.
Whole tyre reclaim	100	100	100	100
Wood Rosin	75	75	25	25
Limed Rosin	25	25	-	-
Slaked Lime	10	10	5	5
Zinc Oxide	1	1	5	5
Vulcafor ZIX	2.4	-	1	-
Vulcafor ZDC	3.6	-	2	-
Sulphur	-	6	-	4

The compounds are mixed on the roller mill and are then dissolved in a suitable solvent such as petroleum, solvent naphtha, or tri-chlorethylene, to form solutions containing 35% of solid. The solutions are stable when left separate and either A and B, or C and D, are mixed in equal proportions immediately before use. The resulting masses, after evaporation of the solvent, will cure at room temperature in the course of 3 to 4 days, becoming hard, elastic, non-thermoplastic and free from tackiness. These cements adhere

strongly to many types of surfaces, including metals and vulcanised rubber. The mixed solutions have other possible applications, and can be used for waterproofing or as acid-resistant coatings. The composition may, in that case, be modified by the addition of softeners such as pine tar, mineral oil, or by reducing the rosin content.

CHAPTER VI.

Rubber Cements.

THIS subject has already been dealt with in Vol. I, page 169.

There are a good many difficulties in connection with the manufacture of a self-vulcanising cement, so that one can almost say that there is actually no such thing.

It may be pointed out that a self-vulcanising cement cannot be packed by itself as obviously it would vulcanise during storage in its own package. Therefore, one can be quite certain that no cement in a single solution can be self-vulcanising. By "self-vulcanising" it is meant that vulcanisation will carry on to a reasonable degree at room or normal temperature.

The method of making a reasonably satisfactory self-vulcanising cement is to use two cements and to mix them just before use. Preferably, one cement, should be of a different colour or appearance from the other so that it is easy to avoid errors in mixing. One cement can contain the sulphur and the other the ultra-accelerator. As long as these two cements are kept separate they can be stored for an indefinite period. As soon as they are mixed, however, vulcanisation will proceed

slowly even at room temperature. The attainment of a good degree of vulcanisation in a reasonable length of time is extremely difficult. It must be pointed out that if vulcanisation is to continue automatically at room temperature, and give a good degree of vulcanisation in two or three days, this vulcanisation will continue, and if extra sulphur is present, in another two or three days we have over-vulcanisation and at a later date, still further vulcanisation, which will continue as long as free sulphur is present. On the other hand, if we curtail the sulphur content merely to that needed for vulcanisation, then we find that the cure proceeds very slowly, and instead of getting a cement that will give us a reasonable degree of cure in two or three days, we find that several days are necessary. Practically, an adjustment between these two extremes is made so that self-curing cements will over-cure but will give a reasonable degree of set-up in two or three days.

There are many other factors in connection with the making of a self-curing cement. We can take such a mixture containing a rubber soluble accelerator and, naturally, rubber soluble sulphur. If we apply this cement to a piece of glass, let the solvent evaporate, we find that in two or three days we have attained a fair degree of cure. If, however, we apply this cement to rubber, we may find that at the end of even six or eight days no cure at all is obtained. This is because the sulphur or accelerator is soluble in the rubber, and has migrated or travelled from the cement to the other compound. If, on the other hand, the other compound is a blooming stock containing a large quantity of excess sulphur, this sulphur content will be balanced, and some will always remain in our cement. At the present time rubber compounds are generally non-blooming, so that our cement will gradually lose its sulphur. If the

accelerator is soluble, this also will migrate, and our accelerator strength will rapidly decrease. The best answer to this is to use a non-soluble accelerator, or a non-migrating one, such as the "Zinc Salt" of an ultra-accelerator. The "Ultra Zinc DMC" should, in this case, be the right type to be used for this purpose.

By using the Monsanto's "RN-2 Crystals," which is readily soluble in naphta, benzole, and other solvents the necessity of having two distinct mixes—one containing the sulphur and the other containing the accelerator—can be obviated, as a solution of this accelerator can be added directly to the to be self-vulcanising cement, already containing sulphur and all the other ingredients, saving thereby time and, consequently, money.

The Right Solvent for Rubber should consist of a distillate of coal tar, free from other substances, including water, should be clear, colourless and of good odour.

On examination the Coal-Tar-Naphta must show:-

(a) that the specific gravity at 15.5° C. (60° F.) is not more than 0.870;

(b) that when the material is distilled at a rate of from 4 to 5 cc. per minute—which is apparently 2 drops per second—there distils at or below 120° C. not more than 5% by volume and at or below 155° C. not less than 95% by volume;

(c) that when about one gram of the material is exposed to the air, in a flat bottomed glass dish, about 3" in diameter at a temperature of 60 to 65° F., in a place free from draughts, it volatilizes completely;

(d) that the material does not contain carbon-disulphide in excess of 0.1% by weight;

(e) that the material is free from naphthalene, phenolic bodies and pyridine bases;

(f) that on incineration, the ash of the material does not exceed 0.01%.

Comparative time of Evaporation of certain Solvents

The following figures give the relative rate of evaporation of five cubic centimeters of the solvent, contained in a Petri dish $3\frac{1}{2}$ " in diameter, $\frac{3}{8}$ " in height, inside measurements.

1. Carbon Bisulphide	4 minutes
2. Acetone	4 "
3. Chloroform	7 "
4. 70°-72° Gasoline	8 "
5. Carbon Tetrachloride		9 "
6. Pure Benzol	10 "
7. Benzol 100%*	11 "
8. Benzol 90%*	13 "
9. Benzol 50%*	22 $\frac{1}{2}$ "
10. Pure Toluol	29 "
11. Commercial Toluol	31 "
12. Solvent Naphta	115 "
13. "Motor" Gasoline	124 "
14. Turpentine	200 "

* 100% benzol is a commercial benzol all of which distils over up to 100°C. 90% benzol is one 90% of which distils over up to 100°C.; similarly, 50% of 50% benzol comes over up to 100°C. They are not pure benzene, but mixtures of benzene with toluene and higher homologues in varying proportions.

Proportions of Solvent for various Solutions.

Solution for Ground

Sheets 50% on the weight of dry solution.

Solution for Paulins	50%	„	„	„
Solution M 2	30%	„	„	„
Solution B 1	58%	„	„	„
Solution A - 110	52%	„	„	„

Quantity of solution to be applied on canvas for various fabrications.

Standard Ground Sheets:

a) Muslin	9 - 4½ oz.	per sq. yd. in	3 coats.
b) Sheeting	9 - 4½ oz.	„ „	3 „
Khaki Ground Sheets	8 oz.	„ „	2 „
Jute Ground Sheets	10 oz.	„ „	3 „
Paulins	11 oz.	„ „	4 „
Insertion Sheetings and Rubber Hose canvas coated with M 2	9 oz.	„ „	1 „
„ „ A - 110	13 oz.	„ „	1 „

CHAPTER VII.

Aluminium, an Ideal Metal for the Rubber Industry.

IN Vol. I, a chapter is devoted entirely to the moulding of rubber goods, but it is not stated from what metal the moulds should be made. If copper was not the born enemy of rubber, that metal could have been chosen especially because of its great ability to conduct heat. Steel could have been chosen also but for the fact that it rusts under the action of steam and even in moisture of the air. Glass is absolutely immune from the action of any known chemical, and were it not for its brittleness, it would be an ideal material with which to make moulds.

No perfect metal has yet been found, and for the time being we have to content ourselves with any metal which, though not perfect, has as many qualities as we can reasonably find assembled in one and the same body. We have such a metal in Aluminium, which embodies many of the required qualities. Aluminium is not heavy, its specific gravity is far below the specific gravity of copper and many other metals. It is white and can be polished. It is unaffected by steam, water, and chemicals with the exception of hydrochloric acid, chloride of sulphur,

lime, and the salts of mercury. Aluminium is not affected by rubber, nor sulphur, nor rubber solvents, nor most of the fillers used in the process of manufacturing rubber. In addition, it is a good heat conductor, is strong, and as such can be used as mandrels for building up rubber hoses, also as rods and bars on which to vulcanise ebonite tubes, and as sheets for making drums on which to vulcanise rubber sheetings. Aluminium sheets may also serve to cover wooden tables and shelves, thereby avoiding any wooden particles being incorporated in rubber compounds.

The above remarks concern only pure aluminium, but when aluminium of more strength is required—for producing moulds for instance—an aluminium alloy should be made use of, the strength of which should not be less than 20 tons per sq. inch. This alloy should contain a certain percentage of copper with the addition of small quantities of zinc and silicon, and would even be cheaper than pure aluminium. As for a foundry, there is no difficulty for casting aluminium alloys. They melt at a temperature of about 600°C , and can even be cast, on the spot in the Rubber Factory, where it is always possible, in the smithery, to obtain such a temperature, whereas iron, cannot be melted in the smithery because it has a melting point of 1375°C . The solidity of cast aluminium alloys is comparable to that of cast iron, except that the former is considerably softer and less brittle than the latter, and cast aluminium moulds conserve the qualities of pure aluminium. They can be well polished, are light, will continue to possess the remarkable heat or cold conductivity of the aluminium and preserve their power of resistance to rust. Aluminium moulds can

be used for the manufacture of battery cases, rubber balls, motor horn bulbs, tubes, tyres, etc.

Aluminium alloy can also be used to cast the formers on which to produce dipped goods either from latex, or from rubber dissolved in solvents, such as gloves, teats, and the like.

Even in Rubber the Plantation, aluminium trays are recommended, so that it can be said that aluminium is the ideal metal to be used for all purposes in the Rubber Industry.

Comparative Properties of Aluminium and a few other Metals.

	Spec. Gravity.	Weight per Cubic Inch in Lbs.	Melting Point in °C.
Aluminium Pure	2.705	0.098	658.7
Aluminium Alloy	2.950	0.106	615
Cast Iron	7.220	0.260	1375
Copper	8.890	0.320	1083
Lead	11.400	0.411	327
Mild Steel	7.860	0.284	1530
Nickel	8.670	0.312	1452
Tin	7.400	0.268	232
Wrought Iron	7.700	0.278	1550
Zinc	7.190	0.259	419

Chemical Reaction on Aluminium.

A. Substances having no, or very slight, action.

Acetone	Ammonia	Barytes
Alcohol	Ammonia Carbonate	Calcium Carbonate
Alum	Balata	Calcium Dioxide

Calcium Bi-sulphide	Lithopone	Resins
Carbon Tetrachloride	Litharge	Sulphur Dioxide
Coal Tar Nephta	Magnesium Carbonate	Stearic acid
Glue	Nitric acid	Sulphur
Glycerine	Oils	Talc
Hydrogen Sulphide	Paraffin wax	Whiting
Kaolin	Rubber	Zinc oxide
		Zinc Sulphide

B. Substances having vigorous action

Chloride of Sulphur	Lime	Potassium Hydrate
Hydrochloric acid	Potassium Carbonate	Sodium Carbonate
		Sodium Hydrate

International Atomic Weights

		Symbol	Atomic Weight	Principal Valence
Aluminum	Al	26.97	3
Antimony	Sb	121.76	3, 5
Arsenic	As	74.93	3, 5
Barium	Ba	137.36	2
Bismuth	Bi	209.00	3, 5
Cadmium	Cd	112.41	2
Calcium	Ca	40.08	2
Carbon	C	12.00	4
Chlorine	Cl	35.457	1
Chromium	Cr	52.01	2, 3, 6
Cobalt	Co	58.94	2, 3
Copper	Cu	63.57	1, 2
Fluorine	F	19.00	1
Gold	Au	197.20	1, 3
Helium	He	4.002	0
Hydrogen	H	1.008	1
Iodine	I	126.932	1
Iron	Fe	55.84	2, 3

		Symbol	Atomic Weight	Principal Valence
Lead	Pb	207.22	2, 4
Magnesium	Mg	24.32	2
Manganese	Mn	54.93	2, 3, 7
Mercury	Hg	200.61	1, 2
Nickel	Ni	58.69	2, 3
Nitrogen	N	14.008	3, 5
Oxygen	O	16.000	2
Phosphorus	P	31.02	3, 5
Platinum	Pt	195.23	2, 4
Potassium	K	39.10	1
Silicon	Si	28.06	4
Silver	Ag	107.880	1
Sodium	Na	22.997	1
Sulphur	S	32.06	2, 4, 6
Tin	Sn	118.70	2, 4
Titanium	Ti	47.90	4
Tungsten	W	184.0	6
Zinc	Zn	65.38	2

Remarks:— *Formers for Dipped Goods* from latex or rubber dissolved in solvents, instead of being made of aluminium, can also be made from a special timber called Veempai which is available in Trichur, Cochin State, and also from two other varieties of wood called “Kumpil” and “Paera”. Formers made from the above named woods are shaped on the lathe in the required form, after which they are waxed, polished with hard wood, and then dipped a few times in acetic acid so as to impregnate them. The formers are then ready for the dipping process.

CHAPTER VIII.

Latex.

IN Volume I, we have discussed the theory of Latex and also the various accelerators and chemicals which may be combined with it. We have always to bear in mind that latex being a colloid, the accelerators and chemicals to be incorporated in it must be of a colloidal nature. It has been stated that latex is used either in its normal form as it comes from the tree, or in concentrated form. In the former case its rubber content varies from 35 to 42%, and it is preserved at the plantation with ammonia. From the normal latex, the concentrated one is obtained by different processes. By the Centrifugal Process one obtains a latex with a rubber content of 60 to 63%; by the Creaming Process, i. e., by adding to latex such organic colloids as Gum Karaya, Gum Tragacanth, Locust Bean Gum, Alkali Alginates, Pectins, and the like, one obtains a rubber content of about 58%; whereas by the Evaporating Process (Revertex), the rubber content is about 70 to 72%.

There is still another form of latex, *the vulcanised latex*, called *Vultex*, in which the rubber particles are vulcanised in suspension, which, on drying, produce a cured article without further application of heat. This

type of latex has practically no tendency to over-cure, or thicken in storage, and may be obtained in solid content of 65%, and in viscosity up to a heavy paste of dough.

Monsanto have communicated to us the results of their laboratory tests and researches on latex, which will appear in the following pages, in addition to our personal notes.

Liquid Latex.

The rubber-containing milk of "Hevea Brasiliensis", as obtained from the trees by tapping, consists of a dispersion of minute rubber globules in an aqueous solution or serum. The globules are in rapid Brownian Movement which ceases when the latex is acidified; and the globules then coagulate by separating from the serum in clots. The globules are 0.5 to 3 microns* in diameter and vary from egg-shape to pear-shape. According to Hauser they consist of a viscous liquid surrounded by a tough elastic film and an outside layer of protein and resins. The specific gravity of fresh latex runs from 0.967 to 1.000, the rubber content varying from about 45% to 17%. Normal latex contains about 33% of rubber and has a specific gravity of about 0.983. To preserve it and permit its transportation from the plantation to other places, latex is treated with 2 to 5% of concentrated ammonium hydroxide so that, when used in the factory it usually contains from 0.5 to 1% of ammonia as NH_3 and has a pH value of approximately 10 to 11.

Examination of Latex.

Sampling. The latex must be thoroughly agitated before drawing samples. Since this is virtually impos-

* 1 micron = one millionth meter = 0.001 millimeter.

sible when the latex is stored in a tank, samples for analysis should be taken from the top, middle, and bottom of the container. When the latex is stored in a drum, the best method to obtain thorough agitation is to remove the bung and stir violently with a $\frac{3}{4} \times 1\frac{3}{4}$ inch paddle, as rolling a full drum along the floor for hours does not stir up the sediment nor produce a uniform mix.

Colour. The latex should be white to bluish white. A yellow to cream shade indicates the use of bleaching agents, which decrease the stability of the latex and produce poor ageing.

Sediment. No sediment should be present as judged by allowing 100 cc to stand overnight in a graduate.

Odour. The latex should be free from putrefaction or chlorine. Sodium hypochlorite is sometimes used to destroy the odour of putrid latex.

Copper or Manganese should not be present in quantities above 0.001 %, as judged by ignition of the dry film from the total solids determination and analysis according to standard methods of Chemical Analysis 4th Ed. Scott.

The mechanical *Stability* is judged by the time in seconds required to flocculate 60 cc of the latex in a four ounce square bottle ($1\frac{1}{2} \times 1\frac{1}{2} \times 4$ inches), when agitated by a Hamilton Beach soda fountain mixture at from 10,000 to 15,000 R. P. M. at a given temperature. *Motor speed and temperature are very important.*

The stability against zinc oxide is determined by adding a definite quantity of colloidal zinc oxide based on the solids content of the latex and noting its decrease in mechanical stability. Another method is the determination of the quantity of zinc oxide required to

flocculate the latex when heated to some elevated temperature of 60 to 80°C.

Total Solids Content (T. S. C.). Dry overnight at 60°C approximately 10 grams of the latex, weighed in tared petri dishes to the nearest milligram. Turn the films in the morning and dry to uniform colour or constant weight.

A quick but very accurate method, when the technique is acquired, is to weigh approximately 3 grams of the latex in tared petri dishes, manipulate the dishes to flow a uniform thin deposit over the entire bottom, dry 1 to 2 hours at 100 to 105°C.

Dry Rubber Content (D. R. C.) Weigh accurately (15 to 20 grams of 60% latex or 20 to 25 grams of normal latex) in a weighing tube, transfer to an evaporating dish, dilute with several volumes of water and coagulate with 1% acetic acid. Heat one hour on a water bath or until the coagulum gathers on the surface, leaving a clear liquid serum. Remove this coagulum, wash with distilled water and treat as follows:

1. Wash several times with distilled water passing through squeeze rolls between washings; dry at 60 to 70°C and weigh.

2. Break up in small crumbs, place in 600 cc beakers with about 400 cc of distilled water, boil, changing water every half hour for 4 to 6 hours; wash carefully with distilled water, dry at 60 to 70°C and weigh. This method gives the lowest and nearest value for dry rubber content.

Water soluble constituents = T S C minus D R C.

Ammonia. (a) *In the absence of fixed alkalies, soaps and wetting agents*, weigh carefully 10 to 15 grams of the latex in a glass stoppered weighing tube, transfer

to a 400 cc beaker and dilute immediately with 10 to 15 volumes of water, carefully rinsing out the weighing tube at the same time. Titrate with any standard acid using methyl orange or methyl red indicator. Normality multiplied by 1.7 equals per cent ammonia by weight.

(b) *In the presence of fixed alkalies, soap and wetting agents*, distil the ammonia off into a known excess volume of standard acid. Titrate the excess acid with standard alkali. Total alkali may be determined as in (a), the ammonia as in (b) and the total fixed alkali such as NaOH, etc., soaps, wetting agents, by the difference (a) minus (b).

Ash. Ignite a sample of the dry film from total solids content determination. The ash is based on the total solids content and not on the dry rubber content.

Viscosity. The Stormer or Hoesppler viscosimeters are satisfactory, the latter being preferred for accurate determinations, but it is too delicate for plant control. Many simple and satisfactory "home made" viscosimeters are giving good results for plant control, their principle being based on the time in seconds required for a definite volume of latex to flow through an orifice. Since a slight variation in temperature produces a considerable change in viscosity, all determinations must be carried out at some convenient uniform temperature.

Flow. The time in seconds required for a definite volume to flow an arbitrary fixed distance down a glass plate set on a 45° incline at a standard temperature.

pH. The glass electrode as supplied by several instrument manufacturers is satisfactory. However, for approximate results, the Wulff instrument is convenient, and indicators such as the B. D. H. (British Drug Houses Ltd.) Universal Indicator may be used.

Wetting properties. A good and simple test is as follows: Prepare a 2% aqueous solution of the wetting agent and add to an equal weight of 40% latex. Drop one inch lengths of tyre cord carefully on the clean surface of this latex. The time in seconds required for the cord to disappear is taken as the wetting time. *A good wetting agent should have a value of not over 5 seconds.*

This test should be carried out on a freshly prepared wetting agent 20% latex mix, then allow the mix to stand several hours or possibly overnight, and recheck. A marked increase in wetting time indicates coagulating ions are present in the wetting agent, causing a loss in the stability of the latex. *The Draves method is satisfactory for aqueous solutions of wetting agents but is not adaptable to latex.*

Surface Tension. The *DuNouy Tensiometer* is a convenient and satisfactory method for surface tension measurements. However, it produces erroneously low results when an unstable oil emulsion has been added to the latex, and similarly high results when the latex has been artificially thickened or contains large quantities of soaps of the higher fatty acids. Surface tension measurements, like viscosity and flow, must be carried out at a standard temperature.

Surface tension gives an indication of the wetting properties of a latex compound, but cannot be correlated with actual practice. Many latex compounds containing wetting agents with surface tension of 34 dynes per sq. cm., give faster wetting than those with surface tensions of 31 to 32 dynes per square centimeter.

As we have already stated in Vol. I, since latex compounding is carried out in the liquid state, all ingredients must be brought together in the form of

aqueous solutions, emulsions, or dispersions. These ingredients, as well as the latex itself, must be reasonably stable, and must be compatible with each other in order to avoid processing difficulties. While latex acceleration follows the methods used in dry rubber compounding, the use of standard rubber compounding ingredients must be carefully chosen, the selection being based on sound latex technique.

Stabilizers. Latex is a relatively unstable material, and the addition of compounding ingredients must be accompanied by the use of *stabilizers*, either in the dispersion of the compounding material or directly in the latex.

The common stabilizers are water-soluble materials such as ammonium caseinate, glue, soaps, NaOH, KOH, Na_3PO_4 , gums and wetting agents (sodium salts of organic sulfonic acids). Wetting agents increase the foaming properties of the latex and lower the surface tension, while all stabilizers, with the possible exception of Bentonite, increase the water absorption of the finished product, and give a greasy feel to the dry film.

It must be remembered that there is no universal stabilizing agent. One must be chosen which best serves the purpose, and the selection is determined by latex practice.

Ammonium caseinate is an effective stabilizer, giving a slight increase in viscosity, but showing appreciably no effect on cure, ageing, or general physical properties when used in quantities up to 1% on the rubber content of the latex. Quantities above 1% on the rubber must be accompanied by a preservative such as boric acid, "Santophen 20S," phenol, etc., to prevent mildewing of the dry film.

Glue is a poor stabilizer and should not be used in dipped goods because it migrates to the under side of the film and builds up a deposit on the former. However, glue is effective in securing a good anchorage of rubber to animal fibres such as mohair. Preservatives such as "Santophen 20S" must be used with glue to avoid mildew and putrefaction. Fixed alkalies such as NaOH, KOH, etc. *should only be used as a last resort and then in minimum quantities, because they impair the ageing properties of the rubber and generally activate the cure.*

The common wetting agents are very effective stabilizers, some increasing the foaming properties immensely and others having very little effect. They are used in small proportions on the rubber, 0.10 to 0.25 % and never over 0.5 %. A mixture of 0.10 % of the wetting agent "Santomerse" (dry "Santomerse" based on the wet weight of the latex) with 0.1 % NaOH or KOH is a very effective stabilizer and is inert in ageing tests up to 0.25 %.

Soaps such as sodium or potassium oleate, triethanol amine oleate, etc. *are not generally used, because their undesirable property of increasing the water absorption of the rubber. They have been replaced by wetting agents.*

The stability of latex towards zinc oxide may be increased by removing or reducing the ammonia content, and preserving with a small quantity of caustic plus a wetting agent.

Acidic accelerators of the mercaptobenzothiazole type tend to reduce the stability of latex, and require special stabilization with large quantities of caustic alkali, thus impairing the ageing properties and water resistance of the finished product. It may be desirable

to find another accelerator, which can be a derivative of mercaptobenzothiazole that does not reduce the stability of the latex.

Removing or reducing the ammonia content of latex increases the stability toward acidic accelerators and zinc oxide. As a matter of fact the thickening and subsequent coagulation of latex, that is attributed to acidic accelerators, is negligible in the absence of zinc oxide. Removing or reducing the ammonia content reduces the formation of the zinc-ammonia complex ion which produces coagulation.

The ammonia is removed or reduced by aeration, aeration and heat, or generally, by the careful addition of formaldehyde, forming hexamethylene tetramine which at latex curing temperatures has no effect on the rate of cure.

The latex is first stabilized with alkali and protective colloides, the alkali being KOH, NaOH, Na_3PO_4 , while the protective colloids are generally the common wetting agents, although glue is frequently used. The proportions of these stabilizers vary according to the latex, current practice being 0.10 to 0.25 % each on the rubber content.

A simple method to determine the quantity of 40% (commercial) formaldehyde required to remove or reduce the ammonia is—weight of latex times % NH_3 , to be removed times 6.9 equals weight of 40% formaldehyde. One-half to two-thirds of the required quantity of 40% formaldehyde should be added slowly and with thorough agitation. The remainder should be diluted with an equal volume of water, and added slowly in order to avoid a localized coagulation.

In practice it is preferred to leave about .05% of ammonia in the latex as a safety measure. Materials such as casein, gelatine, etc. must be added to the latex after the ammonia is reduced with formaldehyde, because they react readily with formaldehyde.

The removal or reduction of ammonia helps in the prevention of "webbing" in dipped goods. Where the article is produced by a two-dip-process, ammonia above 0.10% will always show a "feathering off" of rubber in the coagulant.

Thickeners. It is frequently necessary to increase the viscosity of latex mixes by artificial methods. This is necessary in normal latex compounds to decrease the penetration, and in concentrated latex compounds to produce a paste or dough. Karaya Gum, alkali alginates, and Bentonite are in general use while casein, gelatine, locust bean gum, Gum Tragacanth, glue, etc. are also effective.

With the exception of Bentonite these materials increase the hygroscopic properties and mildewing tendencies of the dry film. Bentonite, on the other hand, reduces the stability and adhesion of the latex. The mildewing is overcome by the use of antiseptics such as "*Santophen 20S*" phenol, boric acid, in about 2% based on the gum.

Solutions of these materials are prepared as follows:

Karaya Gum	3 lbs.	} Beat smooth and add
Water—150 to 180° F	70 lbs.	
Water—cold	15 lbs.	
Then add soda ash	12 oz.	} Beat smooth and add
Trisodium Phosphate	1 lb. 8 oz.	
Water	9 lbs.	
"Santophen 20S" (10% sol.)		12 oz.

Use 10 to 15 parts of this Karaya Gum solution in 100 parts of normal latex (wet weight).

Locust Bean Gum	16	} Beat smooth while water is hot.
Water 180 to 200° F	100	

Locust bean gum is coagulated by all acidic preservatives, and since it has little tendency to mildew no preservative is used. Add this gum to the latex carefully while hot, and use a sufficient quantity to produce a high viscosity, since otherwise the latex will cream. This gum is very useful for the preparation of spreader doughs from concentrated latex. Casein will not produce a high viscosity latex unless used in excessive quantities, thus producing a very stiff film. It does, however, improve the bond in adhesives and is used more for this property. Casein solutions vary considerably in formulation depending upon their use.

15% Casein Solution

Water (180 to 200°F)	...	80
Casein (lactic)	15
Ammonia	4
"Santophen 200" (Solution)		1

Add casein to water while stirring, then add ammonia.

The ammonia may be replaced with an equal quantity of borax or one pound of caustic soda and 3 pounds of water. This 15% casein solution is useful in the preparation of pebble or ball mill dispersions.

For thickening latex it is more desirable to use a 25% casein solution made up and used while still warm and in the liquid state.

Casein
Water (180 to 200°F)	68
Ammonia	5
"Santophen 20S"	(10% solution)		2

Piperidine reduces the viscosity of casein solutions, and *Piperidine derivative accelerators should not be used in combination with casein as a thickener.* Sodium silicate and zinc oxide are sometimes used, but it is rather difficult to obtain uniform thickening without varying the formula for each supply of latex. The general procedure is first to add a small quantity of silicate of soda to the latex to act as a stabilizer, then oleic acid (red oil) so as to remove the major portion of the ammonia, then the compounding ingredients which include approximately 5% zinc oxide on the rubber. Finally, add sodium silicate to obtain the desired viscosity.

Since the compounding of latex involves the addition to the latex of dispersions of ingredients which are used as solids in ordinary dry rubber compounds, it is essential that all ingredients should be properly prepared before mixing them with the latex.

Machinery. In order to obtain an aqueous dispersion of many solids, it is necessary to grind the material in water in the presence of a dispersing agent. This can be accomplished by the use of either a colloid or pebble mill. In many cases the cost of the colloid mill is prohibitive and the usual method is by the use of the pebble mill. These mills may be obtained from several manufacturers, and naturally the size and type of mill to be used will vary with the volume of latex and the total amount of ingredients to be incorporated in it. The larger mills are more efficient from the standpoint of quantity of dispersion obtainable

per unit volume of mill, as can be seen from the following approximate figures:

Capacity of Mill in gallons	Quantity of dispersion in grams
1.5	1000 to 1600
2.5	3600 to 4000
6.5	10000 to 12000

It is, however, advisable to have a larger number of smaller units than a few large units, since such an arrangement has greater flexibility and allows the simultaneous preparation of a variety of dispersions.

In general, the instructions as to speed, load, etc. furnished with pebble mills are satisfactory, but listed below are recommendations as to the procedure which will aid in obtaining the best results:

- A. Use a mixture of assorted sizes of pebbles.
- B. Never fill a jar (pebbles included) more than three-quarters full.
- C. Keep viscosity of the dispersion relatively low.
- D. Rotate jars so that pebbles fall freely.
- E. A separate jar for each material saves money, time, and often jars,

Many of the usual compounding ingredients are dry powders, and as such are totally unfit for dispersion in latex. These must be dispersed in water to at least a paste, and it is usually advantageous to introduce them in the form of a dispersion which has a comparatively low viscosity.

Colloidal Sulphur § It is difficult to prepare this material so that it will remain stable over a protracted storage period. It is frequently prepared in a series of two or three mills, each being sufficient for one day's requirements, the mills being kept in rotation. It may be prepared by the following method:

Sulphur (rubber grade)	100	Grind 48 to 72 hrs.
*Dispersing Agent	3	
Water	97	
	Casein	2.5
*Dispersing Agent:	Ammonia	.5
	(or glue	3))

Another method for preparing a good grade of colloidal sulphur is as follows, the sulphur always being stored in glass or stoneware containers,

Sulphur	100	Grind 72 to 96 hrs.
*Dispersing Agent:	6	and then treat
Water	44	as given below

*Darvan, Vultamol, or Blancol.

After about 96 hours grinding remove from the mill and weigh. Each 100 pounds of wet dispersion contains 66 pounds of sulphur, and requires 22 pounds of water to reduce this dispersion to 50% sulphur content.

In 18 pounds of water and one pound of ammonia disperse 3 pounds of Bentonite. Add this to the sulphur dispersion and mix thoroughly. This will produce a relatively stable colloidal sulphur and the

§ *Colloidal Sulphur*, which term is used sometimes in subsequent pages should not be confused with *Colloid Sulphur*, which is a gelatinous mass containing sulphur together with other ingredients for which purpose "*Sulphur Sublimate*" is most suitable; whereas "*Colloidal Sulphur*" is the pure sulphur with no admixtures in a colloidal state of distribution having particle sizes between 0.001 and 0.00001 millimeter.

small quantity of Bentonite will not cloud even the most transparent film.

Instead of Bentonite it is possible to use locust bean gum, or gum tragacanth to stabilize the colloidal sulphur. In this case, use:

20 pounds hot water

1 pound 4 ounces locust bean gum
(or gum tragacanth)

12 ounces formaldehyde

which is to be added to the sulphur dispersion and thoroughly mixed.

Colloidal Zinc Oxide. Tests show that it is better to use a zinc oxide with medium particle size than one more finely divided, as less dispersing agent is required, and after grinding all types show equally good activation. A zinc oxide with low water absorption should be preferred, as it is wetted more easily and a better dispersion is obtained. A dispersion which may be stored from 6 to 8 weeks with only a slight settling is prepared as follows:

Zinc Oxide	100
Gum Arabic	1 Grind 16 to 24 hrs.
Water	99

Any slight setting which may have occurred is easily redispersed.

Colloidal Zinc Sulphide. A colloidal dispersion of zinc sulphide may be prepared using the same formula and procedure as described in the preparation of colloidal zinc oxide.

Carbon Black is a good reinforcing agent in dry rubber, but in latex it acts only as a diluent, increasing quantities giving poorer physical properties. The regular grades of carbon black (channel process) are acidic,

and unless special preparation and treatment are given they will thicken and coagulate the latex. The soft blacks (Castex, Thermax, P-33, etc.) are practically inert in their thickening or coagulating effects. *Carbon black is used for its colour value only, and since it acts as a diluent it is desirable to use a black of high colour value and one that disperses easily.* A carbon black having a low water absorption gives the best pebble mill dispersion, and also a dispersion containing the highest carbon black content.

A low water absorption carbon black may be dispersed as follows:—

Carbon Black	100	
Darvan, Blancol or Vultamol	6	Pebble mill
Water	192	24 to 48 hours
Ammonia	2)

Ordinary rubber grades of carbon black such as Micronex, etc. are dispersed as follows:—

Carbon Black	100
Darvan, Blancol or Vultamol	5
Water	392 to 492
Ammonia	3

whereas soft blacks disperse readily as follows:

Soft Black	50
Darvan, Blancol or Vultamol	2
Water	48 to 98

Clay. The use of clay in latex is limited because it increases the stiffness and dryness of the rubber stock.

The clays used in regular rubber compounds thicken the latex mix, and are so water absorbent that they are difficult to disperse without using an excess of water. However, the non-reinforcing clays such as those used in the paper trade have a low water absorption, and tend to produce a mild reinforcing of latex rubber.

Due to the large quantities of clay used in comparison to the zinc oxide, sulphur, etc. pebble milling costs are prohibitive, and clay is generally added as a slurry prepared with a high speed agitator. When a still better dispersion is required these slurries may be passed through a paint mill, or colloid mill.

Since clays vary in their water absorption, it is difficult to obtain one formula that will be satisfactory. Hence the formula given below may have the water content adjusted for the respective clay to produce a smooth slurry of proper viscosity for latex compounds.

Clay	100
Darvan or Blancol	2
Water	100

Whiting being only a diluent, may be used in large quantities without stiffening the rubber, and is possibly one of the best methods for decreasing the cost of a latex product. Good grades of whiting produce best results when made up into a slurry with water under a high speed stirrer. Pebble milling is possible, but when large quantities of whiting are used the production cost is almost prohibitive. A pebble mill formula is as follows:

Whiting	100
Darvan, Blancol or Vultamol	5
Water	45

This dispersion forms a heavy paste on standing, but thins out on agitation.

Blanc Fixe. When a cheap mix, with high specific gravity is required, blanc fixe is a desirable ingredient. Slurries under a high speed stirrer may be prepared as follows:

Blanc Fixe	100
Darvan, Blancol or Vultamol	2
Water	23

while a good pebble mill dispersions is as follows:

Blanc Fixe	100
Darvan, Blancol or Vultamol	2
Water	48

Blanc Fixe dispersions settle out rapidly and should be prepared when needed. The latex compound in which they are incorporated should also be of high viscosity or kept well agitated.

From the above, it should be noted that fillers are mere diluents in latex compounds, and are used to reduce the cost of the ultimate product. This reduction in cost is questionable, because unless a large quantity of filler is used the saving is negligible, while large amounts of filler impair the physical properties of the latex rubber. Current practice is to use 10 to 25% filler in second grade household gloves, and this is generally a mixture of clay and whiting, the proportions being dependent on the stiffness of the glove. Carpet backing has carried as high as 125% whiting and 75% clay on the rubber.

Monsanto have suggested the following dispersions of their materials for latex compounds.

Pip-Pip. This material is soluble in water up to 5% at temperatures as low as 40°F. The usual procedure is to dissolve it in 10 to 20 times its weight of distilled water at 150 to 180°F. A 5% solution may be prepared and all tests indicate that this solution is still satisfactory after five months.

RN-2 Crystals. The following method is suggested for preparing a 33% emulsion of RN-2 Crystals for use in latex.

RN-2 Crystals	100
Triethanolamine	8
Oleic Acid	15
Water	177

Melt the RN-2 Crystals in a water bath (they melt at about 50°C, or 122°F), add the oleic acid, stir, add the triethanolamine and stir again then, place under an agitator, add about 77 parts of water at 50°C, and follow in a few minutes with the remainder of the water at room temperature. Finally stir until the temperature of the emulsion approximates that of the room.

R-2 Crystals. This accelerator may be emulsified using 15 parts of oleic acid by following the procedure given above. A colloid may also be prepared by grinding in a pebble mill as follows:

R-2 Crystals	100
Bone Glue	3
Water	197

Casein is not satisfactory as a dispersing agent for R-2 Crystals, as the resulting dispersion has a low viscosity which allows the material to settle too readily.

R-23. This material is water soluble, but when used with concentrated latex the solution must be added slowly, and preferably diluted with an equal volume of water to prevent localized flocculation.

Flectol B. This antioxidant which is a viscous liquid can be emulsified by vigorous stirring as follows:

Flectol B	100
Oleic Acid	5
Ammonia	2
Water	93

Flectol H, Flectol White, Perflectol and El-Sixty.

Dispersions of these powders can be obtained by use of the following mixture:

Any one of the above	100
Casein	4
Ammonia	2
Water	94

These materials are ground together in the pebble mill for 24 hours.

Colours. Most colours are easily dispersed.

Colour	100
Darvan or Vultamol	2
Water	298

For gloves the mixture is ground in the pebble mill for 24 hours, and for balloons it is ground for 48 to 72 hours

A-32. This accelerator which is an oily liquid is emulsified in the same manner as Flectol B, using

A-32	100
Oleic Acid	5
Ammonia	2
Water	93

Mineral Oils emulsify quite readily as follows:

Oil	70
Oleic Acid	15
Triethanolamine	5
Water	10

Compounding of Latex. In plants where only one formula is used, it is convenient to disperse all the compounding ingredients together in a pebble mill and add this dispersion to the latex.

Given a dry rubber compound with the following formula:

Rubber	100.0
Sulphur	1.0
Zinc Oxide	2.0
"El-Sixty"	0.5
Pip-Pip or RN-2 Crystals	0.5
Flectol H	1.0
on of ingredients is then prepared th	
Zinc Oxide	2.0
Sulphur	1.0
"El-Sixty"	0.5
Pip-Pip or RN-2 Crystals	0.5
Flectol H	1.0
Casein	0.2
Ammonia	0.2
Water	4.7
	<hr/>
	10.0

Ten pounds of this dispersion per 100 pounds of dry rubber as latex will give the desired dry rubber formula. Similar formulas to suit specific purposes are easily developed.

The choice of acceleration in latex compounding depends upon desired physical characteristics in the finished product, ease of processing, and the actual cost of acceleration. The aim of every compounder is, quite naturally, to obtain the best product at the lowest cost. The means of reaching this objective is a matter of personal choice in many instances, and must of course be based upon reliable experimental data.

Pip-Pip, R-2 Crystals are approximately equal in acceleration. The choice of these accelerators is a matter of personal opinion, and depends upon which

processes best under given factory conditions. Pip-Pip is water soluble, while R-2 Crystals are insoluble in water. Both of these accelerators give good cures with sulphur from 1 to 2% on the rubber at temperature ranging from 180°F to 230°F, but are more commonly used at curing temperatures of 190° to 212°F.

With the base compound,

Rubber as 60% Latex	100
Zinc Oxide	1
Sulphur	1.5

and varying the acceleration thus,

Compound No.

L-588	Pip-Pip	0.5
L-590	R-2 Crystals	0.5

the following data were obtained.

Cured in water at 100°C (212°F)

	Minutes	5	10	15	20	50
	500%	400	510	500	630	800
L-588	700%	1600	1970	2150	2380	3140
Pip-Pip 0.5	Break	3570	4640	5100	5180	5260
	Elong	870	905	880	870	805
	500%	440	510	530	580	820
L-590	700%	1550	1940	2200	2250	3060
R-2 Crystals 0.5	Break	3590	4270	4970	5140	5180
	Elong	860	870	879	860	810

Air cures at 212°F (100°C) will be about 20 minutes slower and have a higher modulus.

Pip-Pip and R-2 Crystals are of the persistent type, giving stocks whose modulus increases with length of cure, but with only slight tendencies toward reversion. Used in proper quantities, with the re-

quisite amount of sulphur, these accelerators yield stocks with very good ageing characteristics. *However, good anti-oxidants should be used whenever possible.*

In general factory practice, especially in the manufacture of gloves, baby pants, bathing caps, etc., the stocks should be cured only enough to enable the goods to strip freely and be handled without distortion, as a short time in storage will produce the extra cure. If cured too tightly when manufactured, the goods will be too stiff and harsh when they reach the ultimate consumer.

"El-Sixty" and R-23 are of little or no value in latex compounds used alone, but when activated with Pip-Pip, R-2 Crystals or RN-2 Crystals they give fast curing stocks with excellent ageing properties at a very low acceleration cost.

"El-Sixty" is non-discolouring, and if properly dispersed, using casein and ammonia, will not thicken concentrated latex mixes.

Since R-23 *is soluble in water* its dilute solution can be added directly to the latex mix. Rated approximately half as strong as "El-Sixty," 1% R-23 is more active than 0.50% "El-Sixty," giving a higher modulus, faster cure, and curing possibly 10°F lower than an equivalent of "El-Sixty."

There are many combinations of Pip-Pip, R-23 and "El-Sixty" in general use, and a few examples are given below. Care should be used with these combinations in a dip tank as they may vulcanize in solution.

	L-687	L-688	L-689
Rubber as 60% Latex	100.	100.	100.
Zinc Oxide	1.	1.	1.
Sulphur	1.5	1.5	1.5
Pip-Pip	0.5	0.1	0.1
"El-Sixty"		1.
R-23			2.

Cured in Water at 212°F (100°C)

		Minutes	5	10	20	30	50
L-687	0.5	{ 500%	350	400	450	470	570
		{ 700%	1550	1770	2110	2290	2610
Pip-Pip		{ Break	3890	4280	4970	4950	4850
		{ Elong	915	905	900	860	870
L-688	0.1	{ 500%	230	260	320	370	420
Pip-Pip		{ 700%	700	1210	1500	1860	1950
"El-Sixty"		{ Break	2030	3240	3730	4310	4150
		{ Elong	945	940	905	905	870
L-689	0.1	{ 500%	510	600	630	730	780
Pip-Pip		{ 700%	1970	2470	2520	2980	3060
R-23		{ Break	5040	5310	5150	4920	5010
		{ Elong	950	915	885	825	820

Ageing 24 hours in solution would have ripened L-688 so much that it would have given characteristics equal to those of L-687. Unless compounds L-687 and L-688 are aged in solution 48 to 96 hours, they are not suitable for curing at 180°F, while a fresh mix of compound L-689 will give good cures at this temperature.

Those using Pip-Pip/"El-Sixty" as above may find the cure slightly on the soft and slow side. They are prohibited from using Pip-Pip/R-23 because of the tendency of the R-23 to thicken the latex mix. This situation may be remedied by substituting for a small portion of the "El-Sixty" an equivalent of R-23. The results are surprising and the thickening can be controlled nicely with only a small quantity of R-23 present.

A small quantity of R-23 (0.1%) added to a 0.5% Pip-Pip stock will show improvement in rate of cure and general physical properties. The use of "El-Sixty" is also an economical method of improv-

The best ageing and possibly the most favorable acceleration for the textile trade is "El-Sixty" 0.5% or R-23 1% and Pip-Pip 0.5% or R-2 Crystals 0.5%, using sulphur 0.75% to 1.25% and usually 2% zinc oxide. The following data are presented for a stock using one of these combinations but with 1% zinc oxide.

L-245

Rubber as 60% Latex	100.
Zinc Oxide	1.
Sulphur	1.25
Pip-Pip	0.5.
"El-Sixty"	0.5

Cured in Water at 100°C (212°F)

Minutes	3	5	10	15	20	40
300%	190	230	240	270	260	290
500%	590	700	810	960	960	970
L-245 700%	2250	2690	3380	3770	3860	3970
Break	5150	5520	5850	5590	5790	5430
Elong.	905	880	840	800	800	785

This compound cures very rapidly and is competitive with RN-2 Crystals or even the "super-ultra-accelerators" for cures as low as 180°F (82°C). Its ageing, as indicated by results from the oxygen bomb, is very good. When this stock is used in textiles, carpets, etc. an anti-oxidant should be used. If 0.75% sulphur is used in this compound, a slightly slower cure results, and a stock is obtained which is no better in ageing.

Numerous combinations of "El-Sixty" or R-23 with Pip-Pip are available. For instance, 1% "El-Sixty" and 0.25% Pip-Pip is not far behind the 50-50 mixture and gives a lower modulus.

RN-2 Crystals. From test data given below it is quite evident that RN-2 Crystals is an exceptionally fast accelerator, giving good cures at low temperatures with low sulphur content. Although RN-2 Crystals tends to vulcanise in solution and tends to thicken concentrated latex mixes to a limited extent, it tends to do these things to a much lesser degree than most of the other "super-ultra-accelerators." Its behaviour in the latex mix compares favorably with that of Pip-Pip. Dry uncured films containing RN-2 Crystals vulcanise very rapidly at room temperature, possibly faster than the equivalent of any other ultra-accelerator.

As series of tests to given below where RN-2 Crystals is compared with Pip-Pip, R-2 Crystals, etc.

Rubber as 60% Latex	100.
Zinc Oxide	1.
Sulphur	1.5
L-515 Pip-Pip	0.5
L-517 RN-2 Crystals	0.5

Cured in Air at 122°F (50°C)

	Minutes	10	20	30	60	120
L-517	500%	480	500	480	470	500
	700%	1630	1700	1660	1620	1670
RN-2 Crystals 0.5	Break	4050	4030	4000	4080	4430
	Elong	935	930	945	930	940

L-515 = Pip-Pip 0.5 — *Not suitable for cures at this temperature.*

Cured in Water at 212°F (100°C)

	Minutes	5	10	20	30	60
L-515	500%	360	360	410	470	520
	700%	1510	1750	2150	2480	2890
Pip-Pip 0.5	Break	3840	3990	4360	4270	4420
	Elong	910	875	820	800	780

	Minutes	5	10	20	30	60
	500%	410	420	440	440	430
L-517	700%	2100	2090	2230	2370	2460
RN-2 Crystals 0.5	Break	5150	4950	4910	4830	4800
	Elong	905	890	845	830	820

R-2 Crystals 0.5% equals Pip-Pip 0.5% in acceleration. However, in the next comparison R-2 Crystals 1% is used as a control for RN-2 Crystals.

Rubber as 60% Latex	100.
Zinc Oxide	1.
Sulphur	1.5
L-561 R-2 Crystals	1.0
L-562 RN-2 Crystals	0.5
L-563 RN-2 Crystals	0.625
L-564 RN-2 Crystals	0.75

Cured in Water at 100°C

	Minutes	3	5	10	20	40
L-562	500%	430	460	540	670	880
RN-2	700%	1570	1860	1970	2610	3330
Crystals 1.	Break	3730	3920	3960	4180	3370
	Elong	905	890	860	720	805
L-562	500%	560	560	590	600	730
RN-2	700%	2180	2190	2290	2500	2740
Crystals 0.5	Break	4670	4420	4090	5200	5120
	Elong	870	850	845	855	825
L-563	500%	610	620	640	700	710
RN-2	700%	2560	2600	2810	3090	3200
Crystals 0.625	Break	5040	5240	5410	5320	5490
	Elong	825	850	855	830	835
L-564	500%	690	710	700	790	910
RN-2	700%	2710	2770	2960	3260	3590
Crystals 0.75	Break	5300	5330	5200	4700	5680
	Elong	855	845	830	820	800

The cure on the R-2 Crystals compound in water at 100°C is about 10 minutes slower than standard, but the data clearly indicate that RN-2 Crystals has about twice the accelerating value of R-2 Crystals, and is more active at low temperatures.

Although RN-2 Crystals may be used with low sulphur, a stock with sulphur below 0.5% does not age well. An example of the strength of RN-2 Crystals is given below.

Rubber as 60% Latex 100.

Zinc Oxide 1.

L-600 RN-2 Crystals 1.0 + Sulphur 0.25

L-601 RN-2 Crystals 0.875 + Sulphur 0.50

L-602 RN-2 Crystals 0.75 + Sulphur 0.75

L-603 RN-2 Crystals 0.625 + Sulphur 1.00

L-604 RN-2 Crystals 0.5 + Sulphur 1.25

Cured in Water at 100°C

	Minutes	5	10	15	20	30	50
L-600	500%	450	370	360	360	320	370
RN-2	700%	1870	1780	1680	1720	1640	1620
Crystals 1.0	Break	4950	4800	4700	4820	4520	4490
Sulphur 0.25	Elong	940	950	940	940	940	940
L-601	500%	490	480	530	530	490	520
RN-2	700%	2350	2310	2390	2400	2370	2320
Crystals 0.875	Break	5480	5220	5350	5310	5220	4960
Sulphur 0.5	Elong	925	905	890	885	880	895
L-602	500%	550	550	590	570	560	600
R-N 2	700%	2540	2770	2770	2680	2690	2640
Crystals 0.75	Break	5450	5550	5790	5620	5500	5470
Sulphur 0.75	Elong	670	655	670	670	900	875
L-603	500%	520	530	570	570	600	600
RN-2	700%	2320	2510	2620	2640	2800	2910
Crystals 0.625	Break	4970	5050	5250	5380	Broke	5250
Sulphur 1.0	Elong	880	860	860	830	Short	845

		Minutes	5	10	15	20	30	50
L-604	{	500%	510	500	530	560	580	590
RN-2		700%	2220	2210	2370	2520	2740	2800
Crystals 0.5		Break	4610	5120	5160	5250	Broke	5770
Sulphur 1.25		Elong	900	900	885	875	Short	880

The above tests favour 0.75% "RN-2 Crystals" for a fast cure with low sulphur content.

"R-23" may be added to RN-2 Crystals compound to hasten the cure and increase the modulus. While a direct substitution of R-23 for RN-2 Crystals does show a saving in acceleration cost, the cure is retarded and the resulting stock is softer. This is clearly indicated in the following data.

Rubber as 60% Latex	100.
Zinc Oxide	1.
Sulphur	1.5

L-683	RN-2 Crystals	0.5	
L-684	RN-2 Crystals	0.5	+ R-23 0.1
L-685	RN-2 Crystals	0.375	+ R-23 0.25
L-686	RN-2 Crystals	0.25	+ R-23 0.5

Cured in Water at 100°C

	Minutes	3	5	10	20	40	60
L-683	500%	450	500	510	560	620	620
RN-2	700%	1990	2110	2280	2390	2740	2790
Crystals 0.5	Break	4430	4660	5150	5110	5060	5060
	Elong	895	815	875	880	860	835
L-684	500%	540	580	570	680	850	860
R-23 0.1	700%	2110	2650	2710	3360	3840	3770
RN-2	Break	4670	4760	4850	5470	5440	5160
Crystals 0.5	Elong	885	835	830	830	795	790
L-685	500%	500	480	650	750	880	780
R-23 0.25	700%	2120	2210	2770	3230	3770	3520
RN-2	Break	4670	4770	5090	5240	5420	Broke
Crystals 0.375	Elong	900	895	850	815	790	Short

		Minutes	3	5	10	20	40	60
L-686		500%	400	450	540	690	870	790
R-23	0.5	700%	1800	1970	2400	3060	3610	3560
RN-2		Break	4660	4880	5280	5290	5240	5210
Crystals	0.25	Elong	920	910	825	835	780	805

From physical tests it is evident that RN-2 Crystals is a fast purpose accelerator, equalling any material on the market on a cost basis. It is easy to use, safe to handle, and worthy of a fair trial where fast cures are required.

For dipped goods where the latex may remain in the tanks for months RN-2 Crystals is not suggested because it tends to vulcanise in solution. However, in plants where the latex is totally replenished once a week, the use of RN-2 Crystals in proper proportions will show substantial savings over Pip-Pip, and is safer to use than combinations of two accelerators, specially where the cure is carried out in air at temperatures not over 212° F.

RN-2 Crystals should be used where a fast cure is required at a relatively low temperature, such as in textiles, paper saturation, etc., the latex being applied and allowed or expected to cure at room temperature.

Anti-oxidants. The "Flectols" are very effective anti-oxidants for use in latex. Good ageing in a stock is not always the result of using a good anti-oxidant, but is brought about by the use of a good anti-oxidant in a properly accelerated stock. The best anti-oxidant fails to produce a good ageing stock if the stock is poorly accelerated.

"Flectol H" is an excellent anti-oxidant for use in latex. It discolours less than any other standard anti-oxidant, and imparts superior ageing qualities to the finished products.

"Flectol B" is a fine anti-oxidant but its use is limited to dark coloured finished products. Many, who do not mind its discolouring action, prefer it to all others since it is a liquid and emulsifies very readily.

"Perflectol" is specially efficient in protecting against copper contamination.

"Flectol White" is non-discolouring and is more efficient than most non-discolouring anti-oxidants. It possesses, in addition, germicidal properties which prevent mildew, thus enhancing its value in some fields. It tends to thicken latex, so about 0.10% NaOH on the rubber should be added to overcome this characteristic.

An interesting comparison of "Flectol H," "Flectol B" and a control stock having no anti-oxidant is given below.

	Rubber as 60% Latex	...	100.				
	Zinc Oxide	1.0				
	Sulphur	0.75				
	Pip-Pip	0.5				
	“El-Sixty”	0.5				
	L-131 Control						
	L-132 “Flectol H”	1.0				
	L-133 “Flectol B”	1.0				
Cured in Water at 100°C (200°F)							
	Minutes	5	10	15	20	30	40
L-131 Control	500%	520	590	560	530	560	450
	700%	2080	2620	2570	2400	2650	2380
	Break	4630	4650	5420	5210	5120	5000
	Elong	885	820	820	850	840	830
L-132 Flectol H 1.0	500%	720	740	710	690	570	560
	700%	2860	3170	3110	2920	2900	2710
	Break	5150	5570	5160	5390	4920	5100
	Elong	840	850	830	845	835	835

	Minutes	5	10	15	20	30	40
	500%	600	640	630	640	660	620
L-133	700%	2550	2710	2730	2770	2810	2740
Flectol B 1.0	Break	2810	5050	4620	4990	5200	4600
	Elong	835	840	800	830	830	810

Laboratory tests also show that the control compound ages well in the oxygen bomb, but melts in the air bomb, while the stocks with anti-oxidant still have good characteristics after 15 hours ageing at 250°F and 80 pounds air pressure. During these ageing tests the specimens were under 50% elongation.

These stocks with anti-oxidants require 21 days to show any deterioration at all in the Geer Oven test at 158°F, and 42 days to obtain a significant test.

Wetting Agents and Stabilizers. "Santomerse" and "Aresklene" are efficient wetting agents for use in latex. "Aresklene" is the most popular, but "Santomerse" has the advantage in being neutral in colour and giving better wetting when only small quantities are used.

"Santomerse" and "Aresklene" are not only good stabilizers, but also reduce surface tension, aid wetting, and increase the foaming or webbing properties of the mix.

"Aresket" and "Areskap" stabilize latex compounds and make very little change in the surface tension, wetting time, or foaming properties of the mix.

The following are the results of determinations of surface tension and wetting time of tyre cord in 20% latex containing "Santomerse" or "Aresklene." These values for wetting time are the average of ten successive determinations for all values under 15 seconds, and

five determinations for all values over 15 seconds. Amounts shown below are for dry wetting agents based on total wet weight of the latex.

Surface Tension (S. T.) in dynes per sq. cm.

Seconds (Sec.) to wet tyre cord.

% in	"Santomerse"		"Aresklene"	
20 %	S.T.	Sec.	S.T.	Sec.
Latex				
2.0	34.0	1.6	32.4	1.15
1.5	34.0	1.8	32.4	1.5
1.25	34.1	2.1	32.7	1.8
1.0	34.1	2.7	33.0	4.1
0.75	34.4	6.6	33.7	47.0
0.50	35.0	83.3	34.3
0.25	35.8	35.4
0	38.4	38.4
H ₂ O	72.3	72.4

It is to be noted that "Santomerse" lowers the surface tension of a 20 % latex less than "Aresklene," but it wets tyre cord more rapidly. It is also interesting to note the sharp break in the wetting curve at 1.0 % with "Aresklene" and at 0.75 % with "Santomerse."

Following are the results of stability-determinations on "Santomerse," "Aresklene," "Aresket" and "Areskap" as judged by the high speed stirrer at 80°C.F. The wetting agents (dry) were used in quantities based on the total wet weight of the normal latex.

	0.05 %	0.10 %	0.25 %
Santomerse	370	720	Foams
Aresklene	335	560	Foams
Aresket	430	830	Foams
Areskap	430	760	Foams
Normal Latex	220 (nothing added)		

Special Materials. "A-32" is an accelerator used only in latex compounds to produce ebonite. It is activated to a limited extent by Pip-Pip.

Santophens 20S is useful as a preservative for casein, glue, etc., about 2% on the casein or glue, being sufficient for this purpose. In adhesives, where the dried cement tends to mildew, about 5% Santophen 20S on the dry content of the cement, or paste, is very beneficial in preventing the formation of the mildew.

Where the adhesive is used under moist or wet conditions, "Santophen 20" is more desirable, as it is only slightly soluble in water and does not tend to wash out.

"Aroclors" are useful in adhesives as they tend to impart special characteristics for special conditions. These materials tend to flameproof rubber films.

Colours. Monsanto have a complete range of colours for use in latex mixes.

A range of insoluble colours has also been prepared by the Imperial Chemical Industries in the form of finely divided water pastes which may be readily incorporated into latex. These products, owing to their small particle size, are ideally suited for the pigmentation of rubber latex mixes, and will give bright fast shades, which are stable under all conditions of vulcanisation. These colours are:—

Vulcafor Orange	AS
Vulcafor Yellow	GS
Vulcafor Green	LS
Vulcafor Red	RS
Vulcafor Blue	AS

Latex Extraction from Guayule.

There are a large variety of plants, shrubs and vines—the American Guayule, for instance—which produce a milky substance consisting of a dispersion of minute rubber globules in an aqueous solution or serum. These minute globules vary in diameter from 0.75 to 3.0 microns, and are in rapid Brownian Movement.

The extraction of latex from these shrubs, vines etc., including of course the Guayule, covered by an U. S. patent to D. Spence, Carmel, Calif., in 1938, is, unlike the tapping method employed for the hevea tree, obtained by crushing the shrubs or the vines between crushing rollers with the help of a buffer solution, maintained at about the same hydrogen ion concentration as that in the juice of the plant, the pH value being, as for the hevea latex, about 7.2. Impurities like sand, bark etc., are removed by filtering the latex, which is concentrated and heated under steam pressure in the presence of a caustic alkali, and then coagulated.

It is said that the guayule latex is more stable towards coagulating agents than the hevea latex, and fine dipped goods can be produced from it, in the ordinary way, whereas when coagulated, it can be worked by employing the same process, with fillers and vulcanising agents, as in the case of any other plantation rubber. It may be mentioned here, that thirty years ago supplies of guayule rubber were delivered to the factory, not in the form of plantation rubber, as at present, but in lumps containing a fairly large percentage of sand and dirt, so that it was necessary to clean them on the Washing Mill in the then existing rubber factories.

General Precautions to be observed in the fabrication of Dipped Goods from Latex.

In part III, Vol. I, the question of using latex in rubber fabrication has been discussed, and further details regarding this important subject have already been given in this chapter.

For the preparation of dipped goods, it is best to use an ammoniated-preserved-concentrated latex of about 60% rubber-content, and in any case should never be less than 55%. For thick articles it may even be as high as 75%. But, when mixes of higher total solid content than 60% are used, some form of heat-concentrated process must be applied to the compound. Viscosity is of great importance. Taking the viscosity of a 60% centrifugally concentrated latex, containing 0.5% ammonia, as being represented by a time of flow of about 9 seconds for 50 cc. to pass through a jet of about $\frac{1}{8}$ " diameter, the viscosity of a mix for the preparation of thin goods by straight dipping (the film being subsequently set either by immersion in coagulant or by drying) should be in the neighbourhood of from 9 to 18 seconds. When pre-treated formers are employed, rather less viscous mixes may sometimes be used, but they are generally not recommended. For very thick goods, correspondingly thicker mixes may be required.

Suitable tanks, as described in the following pages, are to be used for storage, mixing of the latex and for dipping the formers. The composition of the latex compound will be determined by (a) the properties desired for the finished article and (b) the method employed in preparing the latex.

Klein gives the following data:—

Thickness of deposits obtained in one minute:

mm.

- .02 Unconcentrated latex dip.
- .10 Concentrated latex dip.
- .19 Highly concentrated latex dip.
- .40 Concentrated latex thickened with casein.
- .64 Single coagulant dip.
- 1.20 Repeated coagulant dips.
- 3.00 Heat sensitive mix (heated formers).

When working with latex of fixed alkalinity (0.4% to 0.5% ammonia), it is to be noted that while the thickness of the deposit obtained increases only slowly, as the concentration of latex is one of 50%, further concentration of the latex gives a rapid increase in the thickness of the deposit, and this thickness increases proportionately when the viscosity of the latex increases, even though the concentration of the latex remains unchanged. It should, however, be noted that, while relatively dilute latices, which have been treated with thickening agents, will give thick deposits, goods made in this way have a pronounced tendency to shrink or to crack on drying. It is best to work with concentrated latex, the viscosity being still further increased, either by a reduction of the ammonia content, or by small additions to the rubber of say from 0.2 to 0.5% of casein or from 0.1 to 0.2% of gum karaya. The addition of small amounts of thickening agents to increase the viscosity of the latex renders the latter liable to a certain amount of "creaming," the rapidity depending on the initial solid content of the latex compound. It may be mentioned that many of the "thickening" agents are also "creaming" agents for the concentration of latex. The separation of the constituents in a 60% total solid

content, after a few days' standing, will be almost negligible, but it will be appreciable in a 55% content already after a few hours. This separation must be prevented by periodic stirring, or by using a *circulating tank*. Except when heat sensitive mixes are employed, it would seem preferable to make all but the thinnest goods by the use of a coagulant solution applied to the formers before dipping. Alternatively, the thick deposits obtained by simple dipping in thick solutions may be set, before uneven flow can take place, by plunging the former into a coagulant solution, instead of relying on the more slow process of setting by drying.

According to a patent granted a few years ago to the German firm "Metallgesellschaft", the formation of films, bubbles and foam, during the dipping operation may be prevented by adding to the latex compound, as an aqueous dispersion, a small quantity of wool grease dissolved in rape seed oil.

Formers may have a glazed or unglazed surface in the case of porcelain formers. A glazed surface is essential for obtaining perfectly transparent articles, as in this case both sides of the rubber must be polished, whereas the use of unglazed formers will produce a matty inner surface on the rubber articles.

One of the following coagulants may be used either for coating the formers prior to dipping, or for setting the deposits obtained by the use of untreated formers, as soon as they are withdrawn from the latex compound.

A.	Acetic Acid	30
	Methylated Spirit	70
B.	Formic Acid	15
	Methylated Spirit	65
	Ammonium Acetate	8
	Water	12

C. Calcium Chloride	5
Methylated Spirit	50
Acetic Acid	2
Water	43

In the case of coagulant C, the acetic acid may be omitted, when the presence of this acid is found, under working conditions, to lead to a retardation of the rate of cure of the dried deposit. Methylated spirit is a valuable constituent for coagulant mixtures, because it wets the surface of the formers very easily and overcomes the repellent effect of slight greasiness. It also evaporates readily and makes the dipping compound more viscous. It is recommended to reduce the ammonia content of the latex compound to about 0.1% when acid coagulants are used. In using the solution to coat the formers, the latter are immersed quickly and withdrawn slowly to allow the excess to drain off. They are further allowed to stand for a short period, say one minute, in order to give the solution time to partially evaporate. During this time the formers should be inverted to facilitate the uniform distribution of the coagulant, and then returned to the right position for dipping.

A good example of the use of coagulant-coated formers appears in a patent for the production of dipped goods in which the thickness of selected areas can be controlled. Thus stout gloves may be made with thin palms and fingers. The formers receive a uniform coating of coagulant by dipping in a solution of 500 parts of calcium chloride in 1000 parts of methylated spirit and allowing most of the alcohol to evaporate. The parts of the formers corresponding to the thin portions of the gloves are then treated with a 10% alcoholic solution of caustic potash.

Before drying, the deposit of this coagulum should be washed. The formers are immersed in the latex bath fairly quickly, taking say from 5 to 10 seconds. The withdrawal, however, must be performed very slowly and uniformly, taking from a few to several seconds, according to the shape and surface of the former, the viscosity of the latex, and with due regard for the coagulant which has been used. Coagulant-coated formers should be left in the latex from 10 to 60 seconds before withdrawal.

If a straight dipping process is employed, each layer must be set by partial drying before the next is applied. It is common practice to let drying be complete, which is indicated by the absence of white spots on the film. The film should not become too set, or hard, or dry before redipping, as in that case adhesion between successive layers may be poor, and will adversely affect the strength of the finished article. Care should also be taken to see that the temperature during drying is not such as to cause any premature vulcanisation in the course of drying.

Methods involving the thickening of the latex.

As already stated, latex deposits may be obtained by dipping formers made of glass, porcelain, or aluminium, into ordinary or concentrated latex compounds and coagulating the deposits so formed by heating the former, which also vulcanises the film. This process, in the case of ordinary latex, has the disadvantage of being slow, as a number of coats are necessary in order to build-up an object of the required thickness. Furthermore, the coating before coagulation is in such a state of fluidity that there is danger of flow-marks appearing on the film during drying. In order to avoid

this defect, it is suggested that the latex be thickened before immersion of the formers.

In previous pages we have discussed the question of thickening agents to be combined with latex compounds. According to Sotton, thickening may be obtained by adding to latex of a definite ammonia content from 0.75 to 1% of a certain quality of finely divided zinc oxide. To thicken latex, Teague proposed the addition of certain substances which react with the water-soluble protein constituents such as ammonia, soaps, fatty acids, and certain saponification products. Wescott employs as a latex thickener the reaction product of zinc oxide and hemoglobin. When dry or wet zinc oxide is added to a 30% hemoglobin solution, there is a rapid reaction between the two constituents, causing the formation of a batter like mixture. Heating to 30 or 40° C. accelerates the action. This mixture stabilises and thickens the latex. Theoretically, the process of thickening may be invariably applied to concentrated or natural latex. Obviously, there would be an advantage in the application of this process to natural latex, as the cost of concentration could thereby be saved. In addition to this, a more stable latex compound can be obtained. Unfortunately, in spite of the apparent thickening of the latex, the deposit has a very low rubber content, and produces only a thin film after drying.

A patent has been taken, some years ago, by the Societa Pirelli, which permits the use of natural latex and avoids the difficulties just mentioned. By this patent, natural latex with a 4% of ammonia-content, is heated for a certain time at from 40 to 60° C. and is then allowed to cool down before the thickening and sensitising agents as well as the various other compounding ingredients are added. The latex com-

pound is then more viscous, whereas the compounding ingredients remain more easily in suspension, the deposit thereby being thicker. Thus, if small quantities of salts such as zinc acetate, or lead acetate, are added to a stable latex, a thickening of the product, or an agglomeration of its particles takes place without there being any actual coagulation. This kind of latex can be used to produce dipped goods.

Besides glass-lined dipping tanks, as described on page 367, Vol. I, dipping tanks may also be made of Cypres, Veempai, or Peara wood, all lead-lined or coated inside with an alkali-resisting lacquer, and then waxed. They may even be lined with aluminium sheets,⁽¹⁾ provided the latex compound to be used has a very low alkali-content, say of no more than .5 to 1%. The size of the tank should be such as to make it possible for the formers to be completely immersed. It is advisable not to expose more dipping bath surface than is required for the rack which supports the formers, a clearance of one inch being allowed around the four sides of the rack.

Except when a dipping compound of very high viscosity is used, the tank should be preferably of the *circulating type*, jacketed, so that water may circulate in such a way as to maintain the dipping compound at a uniform temperature, ranging from 45 to 60° F. The tank should thus be made either of aluminium or black iron. In the latter case, the surface above the level of the latex compound must be coated with an alkali-resisting rust-proof paint to prevent the formation of rust which might fall into the latex and

(1) In Vol. I we did not recommend the use of aluminium, as this is possible only when the latex compound, coming in contact with that metal, is of very low alkali-content.

cause trouble. The cooling of the dipping bath is necessary because it prevents any change taking place in the compound, reduces the skimming tendency and retards, if not prevents, any thickening of the latex compound.

The latex should circulate at a constant slow flow, from one end of the tank to the other. This will also help to prevent the skimming of the compound. The circulation of the compound should be maintained throughout the 24 hours of the day, without stop, so that there will be no necessity to cover the dipping tank, even during recess hours. The level of the latex should always be at least 5 inches above the walls of the inner tank, which is really the dipping tank. At one end of the inner tank, and connected with it, is a small circular tank, at the lower portion of which rotates a slow-speed stirrer, helping the latex, in that circular tank, to ascend and causing a flux of the latex compound in the other tank, which overflows on the opposite side, the latex thereby descending to the bottom from where it will again be drawn in by the slow movement of the rotating stirring device.

In case rectangular tanks are used, the skimming of the latex can be performed by means of a blade, preferably of wood, the length of which is equal to the width of the tank, only the lower edge of which, say half an inch, is immersed in the latex compound. By moving the blade from one end to the other, the bath is cleaned of all air bubbles and lumps and a smooth surface of the compound is thus created.

The formers to be used in the dipping tank, as already stated, should be of porcelain, wood (lacquered), or aluminium. In the case of aluminium, the latex compound should be of very low alkali-content.

It has already been said that the alkali-content of a latex compound can be reduced by removal, or neutralisation, of the said content. The removal of ammonia can be effected by blowing air on the latex or by subjecting it to the action of an activated carbon. Ammonia can be neutralised by adding substances which react to precipitate insoluble hydroxides or ammonium complexes. When ammonia has thus been removed, or neutralised, a stabiliser can be added to the latex, which will prevent any tendency of the latex to coagulate and will have a pH value of from 7 to 8. The latex should further be treated with any acidic material to reduce the pH value still further. A 4% of formaldehyde solution added to the latex will reduce that value below 7 and it may even be as low as 5 to 4.

Dipped Goods with Wrinkled Surfaces. Various methods have been employed for obtaining wrinkled surfaces on dipped goods*. This type of surface is often required on rubber gloves. It is produced in latex work as follows:—

The former is dipped first in the latex compound until the desired thickness of the film is attained. When the rubber is still wet, it is dipped in a rubber solvent. The surface of the deposit coming into contact with the solvent becomes swollen, whereas the wet layer beneath is not penetrated by it. The swollen surface wrinkles, and as the deposit dries out, the wrinkles remain on the finished product.

Another method for obtaining wrinkled surfaces is to dip the former in a stable latex compound, then immersing the article in a weak coagulant which breaks the film of latex compound on the former, and

* See "Latex in Industry" by Royce J. Noble Ph. D.

the product shows a wrinkled surface after drying. The so-called "crocodile effect" is obtained by this method.

Formers can also have their surfaces engraved with these peculiar markings, with the result that when dipped goods are produced on such formers, they naturally have wrinkled surfaces inside, which become the outer surfaces when stripped.

The stripping is the final operation in the production of dipped goods; in other words, the article is peeled off the former on which it has been made. Fresh unvulcanised or imperfectly vulcanised latex rubber will stick together very strongly, so that the surfaces can only be separated with great difficulty. Even fully cured surfaces of latex rubber show an inconveniently strong adhesion if pressed into contact. Consequently, some kind of surface treatment must accompany the stripping of the dipped goods from their former to prevent the film from rolling and sticking into wrinkles. Ordinarily, a liberal dusting with French Chalk suffices. It has been noticed that where a calcium chloride coagulant has been used, fully vulcanised goods may be stripped successfully merely by working a little water between the film, and the former. Where perfect transparency is to be obtained, dusting powders must be avoided. Articles may be stripped under hot soapy water and dried without rinsing. Any temporary opacity will disappear when drying is complete.

In the case of special type goods, it may be possible to strip the article before it has been dried and thus greatly increase the output of a given dipping equipment. A recent patent which appears to prove this possibility deals with the stripping of hollow

articles by drawing through perforations in plates, these perforations being too small to permit the deposit to pass through. An example is the preparation of valve tubing. This being of small and even bore with relatively thick walls can easily be pushed off the rod on which it was made. The pre-treatment of the rod with a coagulant would facilitate wet stripping.

Zinc stearate is a useful dusting powder since it is slowly dissolved in the rubber and produces an attractive soft-dull-surface-finish. If, after stripping, and zinc stearate dusting, the articles are reheated for a few minutes (say at 100° to 110° C.) a high surface glaze results, but the feel may tend to be harsh. A peculiarly even-surface-finish may be obtained by dipping the dried and cured articles in a suspension of talcum or lycopodium powder in a volatile rubber solvent. This will also facilitate stripping, but this should not be attempted until evaporation of the solvent is complete.

It is occasionally necessary or advisable to extract the finished articles with hot or cold water for varying periods in order to remove soluble constituents. Excessive amounts of stabilisers, or fixed alkalies, may thus be removed, or if the extraction be performed with a hot alkaline solution, free sulphur may be eliminated. Soaking latex goods for some hours in a concentrated ammonia solution, in order to produce a transparent article, was the subject of a German patent application. Extraction of the finished goods with water is particularly beneficial when vulcanised latex has been used as the dipping compound. The tensile strength, as well as the resistance to subsequent wetting of the goods, is substantially improved by this treatment.

Rubber Threads. These are in fairly large demand. In olden days, rubber threads were produced from raw rubber, either pure or mixed, even from "Gofferdam sheets"⁽¹⁾, then vulcanised and cut to size on the cutting machine. This kind of fabrication is rather costly. They can also be produced on the Forcing Machine. The idea of manufacturing round threads on Forcing Machines first occurred when it was found out that rubber tubes could be made by extrusion. In a British patent delivered to Draeman is given a description of an arrangement for obtaining round threads from a solution of rubber in benzene, which, after drying, was vulcanised by passing through a bath of melted sulphur. Several methods depending on an analogous principle were then proposed, but their application in practice could not be definitely adopted until latex mixes appeared in the industry. It is not surprising that latex should have been suggested for spinning threads of rubber, as it coagulates in a bath of acid in exactly the same way as the solution used in the manufacture of artificial silk.

Description of processes for the manufacture of rubber threads from latex appeared in England and United States at about the same time. In England, Marriott described a method for the manufacture of rubber filaments by the extrusion of latex, or a rubber solution. Rubber thread, usually produced from a latex compound of high solids content, is extruded by air pressure, from a Forcing Machine in a solution of ammonium acetate which performs the double function of coagulating and dehydrating the latex. When the thread is sufficiently hardened in the bath, it is removed, dried and vulcanised.

⁽¹⁾ See Page 235 Chapter X.

Hopkinson, in the United States, was one of the pioneers of rubber thread manufacture by the extrusion of latex mixes.

By the Hopkinson process, a latex of high viscosity is forced continuously, by air pressure, through a narrow tubular orifice, immersed in a coagulating bath consisting of an aqueous solution of an acid. As soon as the latex emerging from the jet comes into contact with the acid, it is transformed into a thread of coagulated rubber which travels through the full length of the coagulating bath and then, when it acquires sufficient strenght, is passed into another bath containing glycerine. The object of this latter treatment is to dehydrate the thread, eliminating the water together with the small amount of coagulant which may be present. After passing through two or three baths of glycerine (the first having a temperature of about 15° C., the second of from 100 to 120° C., and the third of from 125 to 145° C.), the last traces of water and acid are eliminated. The threads then enter a bath of water which removes the glycerine. They are then dried on a heated conveyor belt, and passed through solutions of vulcanising ingredients and accelerators in benzol, or carbon tetrachloride. The threads swell in these solvents, retaining a certain quantity of the vulcanising agents, and are then vulcanised.

Since the appearance of the Hopkinson process, numerous companies have interested themselves in this matter. To the Dunlop Rubber Company is credited a process for the manufacture of rubber threads from latex, which was subsequently operated on an industrial scale. The compounded latex, which is of low viscosity in this case, flows by gravity through a nozzle immersed in a dehydrating and setting bath

consisting of a concentrated solution of salts such as ammonium acetate and sodium chloride. The outlet of the nozzle is directed vertically upwards and its distance below the surface of the coagulant bath is adjustable so that the size of the thread produced may be controlled, smaller threads being made by a deeper immersion of the nozzle in the bath. By reason of its relatively lower density, the thread of coagulated latex floats rapidly to the surface of the bath, in which it is dehydrated, by the osmotic action of the solution, which thus fulfils the double function of coagulant and dehydrating agent. On emerging from the coagulating bath the thread is washed, dried, and vulcanised. It is, of course, possible to arrange for a number of nozzles in the bath. They may be constructed of glass, porcelain, stearite, nickel, stainless steel, or even of aluminium, and should ordinarily be preceded by a filter in order to prevent them from being blocked by impurities in the latex. To avoid distortion on handling, or blistering on drying by heat, it is proposed to employ as the setting bath a buffer of pH value between 5.0 and 6.5, i. e. a mildly acid solution which nevertheless has a tremendous reserve power of neutralising alkalinity. Furthermore, the latex mix should be modified so that it sets readily and uniformly when such a solution penetrates into it by osmosis; actually a compound of a weak acid, such as a fatty acid or colophony with a weak base, such as ammonia or ethanoline, is added. It has been observed that such materials are decomposed by the buffer solutions in question, liberating the insoluble acid, and that latex, blown free from ammonia, is readily coagulated by aqueous dispersions of these free acids. In practice, about 1% of ammonium oleate, calculated on the

rubber-content, is added to the mixture. The following advantages are claimed for the process:—

1. Increased rate of extrusion under standard conditions.
2. Wider range of thread sizes produced from a given jet by varying the depth of immersion.
3. Reduced risk of blocking the jet, since the coagulation, though firm and uniform, does not occur sharply at the very opening of the die.
4. Freedom from porosity due to the decomposition of sulphides or carbonates in the latex by strongly acid solutions.

For the production of threads of $\frac{1}{30}$ th inch diameter, the following mix is suitable, and may be prepared by evaporating under heat, in a suitable appliance, a properly compounded ammoniated latex:—

Rubber	92.5	parts by weight.
Sulphur	2.5	„ „
Zinc Oxide	2.5	„ „
Anti-oxidant	1.0	„ „
Accelerator	0.5	„ „
Ammonium Oleate	1.0	„ „

The total solid content of the concentrate should be 61% and the alkalinity (reduced by evaporation) should subsequently be adjusted by addition of ammonia solution to be equivalent to 0.25 gm. of ammonia gas per 100 gms. of mix. The viscosity at 20° C. should be such that, when 180 ccs. are placed in a cylindrical cup, 5.2 cms. in diameter, with a tubular orifice of 0.318 cm. diameter and 1.4 cms. long, the first 50 ccs. will take 25 seconds to flow into a convenient receptacle. The setting solution has a pH value of 5.3 and contains per litre:—

Sodium Chloride	200	grams
Ammonium acetate	300	„
Acetic Acid	60	„

After remaining in such a bath for 30 seconds, the thread is strong enough to be handled.

A process of general application which may, nevertheless, be applied to the production of extruded latex threads, uses a setting bath of ammonium-sulphate-solution maintained at 85° C. Latex containing zinc oxide (normally added as one of the vulcanising ingredients) rapidly coagulates in a uniform manner through its mass, whereas in the absence of zinc oxide, or an equivalent product, the setting action only progresses slowly inwards from a surface skin.

The level of the liquid in the feed tank should be high enough to allow the thread, as it emerges from the nozzle, to travel for a short distance in the coagulating bath. After a short time, because of its lower density, the thread will rise to the surface of the bath.

The distance travelled by the thread must be sufficiently long enough to ensure satisfactory coagulation and dehydration.

The thread is next put into a hot washing bath and is then passed between two rollers which calender it to some extent, over heated drums, and is finally wound up.

When working with latex, it is necessary to take the following precautions: First, the latex, must flow at constant speed and under a perfectly uniform pressure. This result may be obtained by using nozzles which consist of very long tubes like those employed in the Hopkinson patent. They should be fed with latex at a pressure equivalent to a height of 1 meter of

water, which is kept constant by maintaining a constant level of latex in the feed tanks.

It is important that the latex mix for the preparation of threads should be of high solid content, i. e. about 60%, in order that the coagulum may be mechanically strong.

A simple mix suitable for producing rubber threads is contained in the following formula:—

Rubber (as concentrated latex)	100.
Zinc Oxide	2.
Sulphur	3.
Accelerator	1.

The zinc oxide, sulphur and accelerator are prepared in the ball mill and then incorporated in the latex. The above mix vulcanises in 10 minutes at 150°C., or in 40 minutes at 100°C.

It is quite evident that Rubber Threads made from latex are better than those made from raw rubber. The latter must be cut into threads on the Cutting Machine, a process which presents numerous difficulties, and in most cases the surfaces of the threads are uneven and irregular. By the latex process, however, one can obtain excellent threads which make possible the production of fine rubber fabrics, elastic lengthwise and breadthwise as well. Cotton and Silk can also be immersed in the latex bath for producing latex threads used in the manufacture of surgical goods, upholsteries and the like.

“Latex in Industry”, page 304, describes a method for producing *Rubber Tubings* from latex. The latex compound is extruded into a coagulant bath, so that the external surface of the extruded stream of latex is coagulated, leaving inside a core of latex. This is blown out, leaving a tube of coagulated latex, which

is then dried and vulcanised. Latex may also be extruded through a mouth piece, with an inside mandrel, as used on the Forcing Machine for producing tubings from rubber compounds. This process is rather complicated, as both the inner and outer surfaces of the extruded tube are to be coagulated. It may perhaps be possible to produce a sample in this way for laboratory tests, but cannot be applied to bulk factory production. Tubes extruded in this way are first immersed in an acetic acid bath for the purpose of complete coagulation, then, as in the case of rubber threads, are passed through two or three glycerine baths, and are finally vulcanised. The time, evidently, is not yet ripe for undertaking such fabrication on any big scale. When the rubber manufacturer has once solved this problem, then of course, as stated in Chapter I of this Volume, the entire equipment of the Rubber Factory will undergo a thorough change, and there will no longer be heavy duty mills, complicated calenders, mammoth vulcanisers and presses, but only tanks: tanks for storing the latex, tanks for mixing the latex, tanks for making various dipped goods, and a few ball and pebble mills to grind the ingredients to be incorporated into the latex.

Rubber Teats. Manufacture of these has for long been carried on in the United States. In Europe, the position appears to be less advanced because the public demands glossy teats of the type which is obtained from a solution of raw rubber and vulcanised in sulphur chloride, called the "*Cold Vulcanisation Process*". Such teats always contain chlorine and have relatively poor ageing properties. Bacteria of all kinds may gather in the cracks which appear so frequently.

Gloves. The manufacture of surgical or household gloves from latex is perhaps more delicate than the preparation of balloons, because of their more complicated shape. For instance, care has to be taken to see that the flow of the latex does not lead to a thickening of the rubber at the junction of the thumb and the forefinger, giving rise to any irregularity in appearance and feel. Difficulty is frequently experienced owing to the persistence of films between the fingers as the glove former is withdrawn from the mixture. The presence in the mixture of a small quantity of emulsified mineral oil tends to prevent this. For a "non-drag" surface finish, the glove may be dipped after vulcanisation in a solution consisting of:—

Shellac	5.00	parts by weight.
Borax	1.25	" " "
Water	93.75	" " "

This solution is prepared by stirring the shellac in the hot borax and allowing to cool before being used.

The following is a good recipe for making *Rubber balloons with Vulcafor P*:—

Nonox NS	1.000	part.
Zinc Oxide	1.000	"
Sulphur	1.000	"
Vulcafor P	0.375	"
Vulcafor MBT	0.300	"
Dispersol L	0.600	"
Casein	0.200	"
Caustic Soda	0.100	"
Water (distilled)	5.425	"
Colour	10.000	"

The ingredients must be mixed for the required time in a ball or pebble mill. The despersed paste is

then added to 166 parts of latex containing 1.5 parts of Vulcasteb A Paste.

Cure: 10 minutes in hot air at 212° F.

Here is a typical formula with Vulcafor ZDC adopted for obtaining very "*transparent films*" with latex mixes for high quality "*rubber balloons*":—

Latex	166
Zinc Oxide Active	.	.	0.3
Dispersol Paste	.	.	1
Sulphur	0.75
Vulcafor ZDC	.	.	0.175
Gelatine	1
Castor oil emulsion	.	.	5 cc.

Cure: 30 minutes at 110° C. or 229° F.

It is to be noted that Vulcafor ZDC can also be used as an activator for slower accelerators, such as Vulcafor DPG and MBT.

CHAPTER IX.

Synthetic Rubber.

Thiokol.

SYNTHETIC Rubber is artificial rubber, and is compounded, manipulated and vulcanised in the same way as natural rubber. Both the products are alike in elasticity and mechanical properties. Although Synthetic Rubber has the advantage of having ozone-resisting properties, it has poor electrical insulating power. For this reason it will never entirely replace natural rubber, but will, very likely, tend to widen the field of its applications to rubber-like materials. For instance, a satisfactory ozone-resisting rubber compound has not yet been produced, whereas certain types of Synthetic Rubber have indisputable ozone-resisting qualities. In the fabrication of high-voltage rubber insulated cables, this can be used to advantage by applying a very thin layer of Synthetic Rubber under and on top of the rubber dielectric, in order to protect it from the ozone which is generated when the cable is under high tension, the synthetic and natural rubber compounds bonding together very satisfactorily under vulcanising conditions.

So far, there are only a few varieties of Synthetic Rubbers known to us. "*Thiokol*" is one of them, and Monsanto are the distributors of this product. They

have made available a good deal of information, which is given in this Chapter. According to Monsanto, "Thiokol" is not the name of a substance, but is a coined word which has been adopted as a trade mark. It identifies a series of olefin-polysulphide-reaction products which are the result of experiments conducted by "*The Thiokol Corporation, Yardville, New Jersey, U. S. A.*", a corporation which manufactures and supplies "*Thiokol*" as a raw material to such firms as are equipped to make use of it.

"**Thiokol**" is a distinctly new and different raw material, somewhat similar to rubber, in that it may be worked on rubber factory machinery. It is compounded and "cured" as is rubber. In appearance Thiokol is like a heavy pale crepe rubber, being light translucent, amber in colour, but of a specific gravity of 1.62.

It is not a substitute for rubber. It is not a cheapener nor a compounding ingredient for rubber, and is not proposed as a cure-all for various ills in the Rubber Industry.

It is a substance produced by the chemical interaction of ethylene dichloride ($C_2H_4Cl_2$) and a soluble polysulphide, of which sodium tetrasulphide (Na_2S_4) is an example. It is a definite chemical compound of a high degree of purity.

Products made from Thiokol are flexible and elastic, much the same as ordinary compounded rubber stocks. These products are essentially unaffected by ordinary solvents such as petrol; paraffin oil, fuel oil, lacquer thinner, etc., in addition, they are extremely resistant to oxidation, or ageing, and electrical high tension or corona discharge, besides offering excellent insulation. So the present primary uses for Thiokol compounds are for replacing rubber compounds which

come in contact with oils and solvents, and perhaps for electrical insulation work of certain specific types, details of which will be given later.

Just as roses have their thorns, Thiokol has certain unpleasant properties from a production stand-point. Thiokol itself, as well as compounds made from it, has a pronounced odour which limits its use to industrial application. At increased processing temperatures this odour is greatly increased and facilities must be provided to take care of it. Thiokol compounds must, after curing, be cooled while still under pressure, just as in the production of hollow rubber balls, or else porosity is developed when the pressure is released on hot Thiokol compounds. The compounding and handling of Thiokol, while not difficult, is somewhat different from rubber, and one must not draw conclusions based on the behaviour of rubber under similar circumstances.

The properties and uses of Thiokol can best be illustrated by describing the mixing and working of a typical compound such as the one shown below. This compound will serve as a basis for a brief discussion of Thiokol properties, as well as the effects of the various compounding ingredients, and curing methods.

Compound No. 1605.

Thiokol	100
Rubber	}	As	5
D. P. G.		Master	0.25
Thiuram		Batch	0.10
Zinc Oxide	10
Carbon Black	25
Stearic Acid	0.50
Total				140.85

The actions of the different ingredients in this formula are discussed briefly in the following pages.

The outstanding property of Thiokol is its ability to resist the action of most solvents. This quality makes it far superior to rubber when the material is to be used in contact with oils, petrol, or similar liquids. The table below shows the percentage of swelling in 48 hours at 120° F., when compared with a rubber stock highly loaded with carbon black and glue.

Solvent	1605	"Oil Resisting"
		Rubber
High Test Petrol	0	26.3
Fuel Oil	0	23.3
Paraffin Oil	0	24.0
Lacquer Thinner	0	29.1
Ethylene Dichloride	1.5	30.5
Benzol	2.3	35.3
Drip Oil	1.0	40.9

Note:—Swelling is obtained by determining the increase in length of a test piece 4" long, by 0.25" wide, by approximately .080" thick.

The physical characteristics of the Compound 1605 are:—

Specific Gravity	1.67
Load at 300 % Elongation		740
Tensile Strength lb./sq. in.		790
% Elongation		370
Hardness — (Shore Durometer)			75

The physical properties of Thiokol compounds are to a considerable extent similar to those of rubber. Therefore, where resistance to solvent action, together with flexibility are desired, Thiokol will effectively replace rubber and such other materials as thin metals, leather, cork, fabrics, etc.

The physical properties as regards tensile strength, elongation, etc. of Thiokol compounds when in contact with oils, are far better than those of even the best

rubber stock. While the figures above would tend to indicate that the tensile strength of the Thiokol compounds is much lower than that of rubber, it should be realised that rubber loses as much as 90% of its tensile strength, when immersed in petrol and becomes very tender, so that its abrasive resistance is practically valueless. Thiokol compounds better retain their original qualities.

The tensile strengths, before and after immersion for three months in petrol, at ordinary room temperatures, of 1605 compound are shown below.

			1605
Original Tensile	790
After Immersion	830
Original Elongation	360
After Immersion	350

The oil-resisting rubber stock which started with a tensile of approximately 3,000 lbs. dropped very quickly to less than 300 lbs. tensile and practically no elongation.

Thiokol compounds do not deteriorate (due to oxidation effects) as does rubber. Tests on sheets of Thiokol, a year old, are found to be substantially the same as immediately after cure.

Even in direct sunlight Thiokol does not lose its properties and there is no evidence of suncracking. While ozone will quickly break down rubber, Thiokol is apparently unaffected.

The characteristics of *Thiokol compounds* may be changed to some degree by the variation of the kinds and amounts of ingredients used. The combinations of characteristics for any given application are so varied that it is impractical to give any formula recommendations. Just as with rubber, it will be necessary to

develop compounds properly to fit the need. It may be of value, however, to discuss briefly the action of a few ingredients in the compounds shown.

Rubber.

While Thiokol compounds can be made without rubber, a small amount is recommended as an ingredient, because it is useful from the standpoint of making processing somewhat easier and reducing the tendency to porosity after cure.

A compound containing 5 parts of rubber by weight on 100 of Thiokol is just as highly resistant to solvents as a rubber-free Thiokol stock. As the amount of rubber is increased, however, it will be noted that the solvent resistance becomes poorer. The more severe the conditions, such as activity of solvent, temperature of immersion, etc., the more noticeable will be the swelling and loss of original physical characteristics.

Various solvents have different degrees of action on Thiokol stocks and each compound should be tested thoroughly, in the solvent, under the temperature condition at which it will be used. If the solvent is a severe one, such as benzol, drip oil, ethylene dichloride, or carbon tetrachloride, and especially if the temperature may be above normal, not more than 5 parts of rubber should be used.

10 parts of rubber will give compounds practically non-swelling in applications where crude oils, lubricating oils, petrol and similar solvents are used.

20 parts are sometimes used where solvent action is not too severe, as is the case with the lubricating and fuel oils. For some applications, where swelling is permissible, in order to gain other characteristics (such as greater flexibility at extremely low temperatures),

the 20-part rubber compounds may be desirable. These high rubber stocks should not be used for the severe liquids as indicated above.

More rubber than 20 on 100 of Thiokol should not be considered.

Zinc Oxide.

Zinc oxide, or a similar oxide, is necessary to bring about the cure of Thiokol. While as little as one volume appears to be sufficient to effect this cure, a minimum of 10 parts is recommended. Higher amounts of zinc oxide do not appear to change the rate of cure.

Carbon Black.

Carbon black of the type used in making tyre tread stocks is a valuable pigment in Thiokol compounding. It gives firmer, higher tensile stocks with excellent resistance to solvent action. A minimum of at least 10 parts of black is desirable. As the carbon black content is raised, the stiffness, tensile strength and hardness will increase. Elongation becomes somewhat lower with the more highly loaded stocks.

It will be found that for many types of applications, the 1605 compound, discussed here, is a good starting point. If greater or less stiffness is needed for a given use, the variation of the carbon black content alone is all that is required.

Softeners -- D.P.G. and Thiuram (Tetramethylthiuram disulphide)

The ordinary types of softeners used for plasticizing rubber are not effective in Thiokol compounds. Many organic compounds, however, do soften Thiokol considerably, even when added in small quantities. D.P.G. and Thiuram are examples of such plasticizers.

They do not act as accelerators of time of cure in Thiokol compounds.

It has been found that a combination of D. P. G. and Thiuram in the amounts shown in the 1605 laboratory formula brings about marked softening, without in any way affecting the physical characteristics of the cured compound.

Thiokol without the softeners will not smooth out properly on the mill. It is important to add these ingredients in the manner outlined under milling procedure.

Stearic Acid.

Stearic acid has been found to be a valuable aid in moulding. A compound containing 0.50% stearic acid will come free from the mould much easier than one without. Amounts higher than 0.50% do not appear further to improve moulding conditions particularly.

Curing. Raw Thiokol, on storage, under normal temperature conditions, undergoes a very slow polymeric change that causes a stiffening of the material. Heating Thiokol for a sufficient time at a high enough temperature in the presence of a small amount of a material, such as zinc oxide, permanently inhibits these polymeric changes. While this is the main purpose of "heat curing" Thiokol, it will be found that other characteristics such as tensile strength and elongation have been improved. These changes do not take place when Thiokol is heated alone, but do when zinc oxide, or a similar substance, is present. *Sulphur is not necessary to effect a cure of Thiokol.*

The correct cure of a Thiokol compound depends somewhat on where it is to be used. Obviously, it must have sufficient heating to prevent further polymeric changes. This is the minimum cure allowable.

It has been found that for most applications a cure of from 50 to 60 minutes at 287° F. is most satisfactory.

It has also been determined that cures can be made at steam temperatures higher or lower than at 287° F. (40 lbs.) by properly adjusting the time. If the steam pressure is increased 10-lbs., the curing time can be cut approximately in half. On the other hand, the time must be doubled if the steam pressure is cut 10-lbs.

Processing. In general, the equipment and procedure for making Thiokol products are similar to those used in rubber practice, notwithstanding that Thiokol has some handling characteristics, however, that differ from those of rubber, and these features need to be taken into consideration.

During processing operations there is generated a gas which, even though present in small concentrations, has a noticeable odour and is irritating to the eyes. The gas is harmless and temporary in effect. Both odour and irritation are overcome, in production departments, by hooding mills, calenders, extruders, and using a slight amount of suction on these hoods.

The softeners should first be milled into rubber and these ingredients added to Thiokol as a master batch, according to the following procedure:

1. Start with a cool mill. Pass the Thiokol through the rolls two or three times and then allow it to band on the front roll.

2. Add the rubber - D.P.G. - Thiuram master batch. It will be found that the batch will soften in a few minutes, and will run smooth on the roll. A great deal of heat is not necessary during this softening

operation. In fact, it is desirable to mill as cool as possible since this greatly reduces the amount of odour.

Do not attempt to break down Thiokol alone, without the softeners, by using a tight mill or heated rolls.

3. As soon as the stock is running smoothly on the rolls, add the carbon black, zinc oxide and stearic acid together.

4. Cut back and forth in the usual manner, and remove from the rolls when completely blended. Slab out approximately 50 % thicker than the mould depth.

Storage of Mixed Stocks. No special precautions need to be taken during the storage of compounded but uncured batches. Stocks re-milled, after standing several weeks, handle well in the tubing and calendering operations.

Tubing and Calendering. 1. Compounds can be made sufficiently soft to permit of tubing and calendering operations without requiring excessive temperatures.

2. On warm-up mills, a little heat causes "Thiokol" to become sufficiently plastic for subsequent operations in less time than required for rubber compounds. Due to this quick warm-up, it is possible to keep the amount of stock rolling on the mill to a minimum which, in turn, means that the stock has to remain on the mill only a short time. This is, of course, desirable, specially when the rate of using up the stock from the mill is low because the object being tubed or calendered, is relatively small, as for example, thin hose tubing.

3. If the extruded material is run into or through water, or a water spray, practically all of the odour or gas is eliminated.

4. "*Thiokol*" compounds do not make good frictioning stocks unless a large amount of rubber, or some rosin or pitch is used. This, of course, reduces solvent resistance. A coat obtained by running the bottom rolls of the calender at odd speeds will adhere well to fabric, specially if it is of fairly open weave.

Adhesions—"Thiokol" to "*Thiokol*." The adhesion of "*Thiokol*" to itself is of interest from two standpoints: first, it is desired to have a union of the plies or laid-up parts of raw stocks before cured, and second, it is necessary for the parts to bond during vulcanisation.

Factors Affecting Raw Stock Adhesion. "*Thiokol*" of itself is not "tacky" as is rubber. Coating with cements, or washing with a rubber solvent, does not give a sticky surface. Because such materials are not solvents for "*Thiokol*," they often do more harm than good. Attempts to bring about stickiness throughout the compound by adding tack-producing substances, have not proven successful, because when a sufficient amount of such an ingredient is incorporated, the solvent and physical properties are adversely affected.

"Thiokol" will knit to itself because of its flow properties. The element of time, however, is of more importance than with rubber. Two pieces of "*Thiokol*" that do not stick together immediately will, if allowed to stand under even slight pressure for a period, knit quite effectively.

Naturally, anything that will increase the flow of the raw stock will reduce the time required for a satisfactory bond. Such factors are higher pressures,

or greater softness brought about by lower pigment loading, or by plasticizers. D.P.G. and Thiuram help because they soften, but they do not impart tack.

To Summarize. (a) **Cleanliness** of surfaces to be united is even more important than for rubber, since dust or liquid particles will not penetrate the surface of "Thiokol."

(b) **Solvents or cements** are of no value because they do not act on the "Thiokol" surface.

(c) **Softeners** of the type used in rubber, as tars, oils or greases, are detrimental instead of helpful, because they do not act on the "Thiokol", but rather "bleed" to the surface sufficiently to prevent union.

(d) **Rubber** increase appears to help the plying-up properties of "Thiokol." This may be due, partially at least, to the softer compounds produced by higher rubber.

(e) **Pigments.** For a given volume loading, the kind of pigment used does not appear to be of much importance.

(f) **Time and pressure** are of definite aid in bringing about uncured ply adhesion. Even with some mandrel cured rubber products, it is found good practice to wrap down the object, allow to stand, say, overnight, remove the original tape and then re-wrap. Such a procedure, or some variation of it, is often perfectly practical to consider for the more difficult laid-up jobs of "Thiokol." The time and pressure required are reduced by anything that brings about greater softening, such as more rubber or plasticizer, less pigment loadings or increased heat. It helps considerably, if plying-up can be accomplished during the calendering operation, when the stock is still warm.

Factors Affecting Bonding During Cure. As would be expected, the most important factor in obtaining good cured adhesion is sufficient pressure. The time or temperature of cure seems to have no great effect. With proper preparation there will be satisfactory adhesion when cured under hydraulic pressure.

In open steam, wrapped pieces cured under a pressure of 50 pounds give adhesion except when the compound is too stiff. The points to bear in mind are:

a) *Low-loaded stocks* give best adhesion. Increased pigmentation gradually decreases adhesion.

b) *The kind of pigment* for a given volume loading does not appear to have any noticeable effect.

c) *Higher rubber* betters adhesion. At least part of this improvement is because rubber addition means lower pigment loading.

d) *Higher "Thiokol" plasticizer* does not improve the cured bond.

e) *Stearic acid* does not affect "Thiokol" to "Thiokol" adhesion appreciably.

Adhesions—"Thiokol" to Rubber. The same general principles apply in obtaining satisfactory bonds between "Thiokol" and rubber as discussed for "Thiokol" to "Thiokol."

The nature of the rubber compound itself does not appear to be of great importance, but it is desirable to omit paraffin, or similar waxes, or oils that tend to bloom to the rubber surface. There is a slight advantage if the rubber compound is not loaded too heavily and if it is not too fast curing.

The factors concerning the "Thiokol" compounds investigated and the general effects observed were:

a) *Pigment Loading.* Good bonds are obtained with the usual amounts of pigment loading. If the stock is loaded to the point where it is somewhat hard or tough in the uncured state, there will be a reduction in adhesion.

b) *Kind of Pigment.* Adhesion does not vary to any great degree, when different fillers are used.

c) *Softeners.* Varying the D.P.G. or other softeners does not alter the union of "Thiokol" to rubber.

d) *Stearic Acid.* Has very little effect on "Thiokol"-rubber bonds.

As with "Thiokol" to "Thiokol" adhesions, pressure plays an important part in "Thiokol"-to-rubber adhesion. Press-cured pieces all gave excellent bonds. The differences found with compound variations were in the case of samples wrapped on a mandrel and cured in open steam.

In ordinary rubber practice, when it is necessary to unite two compounds of widely different characteristics, it is often found desirable to use an intermediate binding or tie-in-stock. This same procedure may at times be of benefit for some "Thiokol"- "Thiokol" or "Thiokol"-rubber combinations.

Open Steam Curing. Porosity in open-steam curing is usually due to two factors: (1) moisture and (2) trapped air. There are no products of the vulcanisation reaction that would cause porosity, nor is there enough gas given off by the "Thiokol" itself, at curing times and temperatures, to bring about any difficulty.

1. *Moisture.* There is from 0.3 to 0.5% moisture present ordinarily in a compounded but uncured stock. This amount is sufficient to make the stock porous, unless means are taken to ensure that the pressure

maintained is at all times as great as, or greater than, the steam pressure corresponding to the curing temperature. At the end of the vulcanisation the pressure must be held up until the compound has cooled sufficiently to prevent the water present from flashing into steam. One effective way is to keep pressure in the heater with air while the contents are cooling.

The "Thiokol" cannot be dried completely to eliminate this source of porosity as the presence of moisture is essential to bring about cure.

2. *Air.* "Thiokol" does not absorb air during vulcanisation nearly as much as rubber. There are two general sources of air in "Thiokol" stocks: it is carried by some pigments, or is entrapped during processing operations. As pointed out in previous pages, the highly absorptive carbon blacks behave worst in this respect so that a replacement of at least part of such pigments by the less absorptive blacks like Castex or Funonex reduces porosity.

To keep air out during processing operations, it is desirable to have a stock neither too stiff nor too soft during handling. Calendering is preferable to extrusion. As would be expected, the thinner the calendered strip, the better the results.

Water Curing. Curing "Thiokol" in hot water under pressure gives more satisfactory results than open steam vulcanisation. The methods used in the laboratory is to partially fill a small 18" x 24" vertical pot heater with water, close the heater and put 50 to 60 pounds of air pressure on top of the water. Steam is passed in from an 80 pound line to bring the water up to the 287°F. curing temperature, then it is maintained by means of an immersed steam coil. (After the steam inlet leading directly into the water is closed,

air pressure may be raised if desired.) When the cure is completed, the steam in the coil is cut off and the hot water is forced out of the heater and replaced by cold. During this exchange, the pressure in the heater is maintained. As soon as the article is sufficiently cooled, air pressure is released and the heater emptied.

This method has several distinct advantages over open steam cures:

1. A positive pressure, well over the steam pressure, corresponding to the water temperature is maintained throughout, thus preventing water in the "Thiokol" compound from flashing into vapour.

2. With open steam, the pressure obtained is dependent on temperature—for a 287°F. cure it is 40 pounds. In this method, the water can be at 287°F, but the pressure on the water is fixed only by the limits of the air compressor and heater equipment. Higher pressures naturally produce more solid cures.

3. After-cooling, in cold water under pressure, is rapid and thorough.

Press Curing and Moulding. 1. "Thiokol" compounds are so impervious to water vapour, or trapped air, that porosity will result in the cured articles, unless the product is kept under pressure until it has been cooled sufficiently. In the case of press-cured pieces, this is accomplished by having water-cooled platens. The moulded articles must be cooled down to a point where water will no longer flash to steam on releasing pressure.

2. The stock to be moulded should be somewhat thicker than the cavity of the mould, but smaller in area. This is to allow for plenty of flow to the sides, pushing the air out ahead of the stock. It is desirable

to have a minimum of traps or packets in the stock as air does not escape during cure. This precaution is more important for "Thiokol" than for rubber.

3. Since "Thiokol" flows quite readily, at curing temperatures, it is rather easy to lose pressure unless the mould cavity is of such design as to confine the stock after a certain amount of initial flow. Small overflow grooves, around the cavity, work satisfactorily. Vents leading to the outside of the mould may permit slow but continuous flow, specially in the case of softer stocks, and thus induce porosity.

Briefly, the trick in "Thiokol" moulding seems to be to allow plenty of opportunity to flow in the cavity, then block it off just outside in order to allow pressure to build up.

4. A smooth, shiny surface is obtainable on "Thiokol" articles if the mould used is highly polished and kept clean. A very thin film of a light mineral oil works well as a mould lubricant. Cotton-seed oil, or a weak soap solution, may also be used. Since the moulds are worked cold, care must be taken, when soap solution is used, that no drops of water remain, as they will not evaporate.

A minimum of mould lubricant should be used in areas near any splices that may be necessary. "Thiokol" does not absorb the oil; therefore, films will prevent adhesion and a surface flow crack may show up.

The incorporation of a small percentage of stearic acid in the compound is of considerable aid in the prevention of mould sticking.

Protection of Rubber by "Thiokol". Thin layers of "Thiokol" will effectively protect a rubber stock from the action of swelling liquids. This principle is being

used to improve the service of rubber articles such as certain types of gaskets, rubber hoses, rubber insulated wires and cables etc.

The "Thiokol" compound chosen should of course be one that is low enough in rubber content to prevent the solvent from going through it to the rubber. As a general rule, a "Thiokol" stock that shows little or no swell, in a given solvent, is utilized to shield the rubber from that liquid. For example, 1605 compound does not swell in gasoline, or benzol, and rubber coated with it and then immersed in these liquids is not affected by them.

The method used to determine the above factors is to immerse test discs in gasoline and in benzol. The samples are approximately $2\frac{1}{2}$ " in diameter by $\frac{1}{2}$ " thick. Discs of solid "Thiokol" are compared with others made with an all-rubber insert. The rubber portion is $\frac{3}{8}$ " thick and $1\frac{1}{2}$ " in diameter and is embedded in the disc. This means that the rubber is protected, top and bottom, by a maximum of $1\frac{1}{16}$ " of "Thiokol" compound.

In addition to preventing the diffusion of liquids, tests made on gas permeability indicate that the rate is cut down approximately 85 to 90% when "Thiokol" replaces rubber.

Discoloration of solvent. "Thiokol" compounds immersed in solvents will cause far less discoloration of the liquid than ordinary rubber stocks. Raw "Thiokol" itself does not have any effect, but some compounding ingredients cause a colour to be imparted, especially to the stronger solvents such as benzol. The following factors should be considered whenever it is desirable to keep discoloration to a minimum.

1. Plasticizers. (a) *D.P.G.* A *D.P.G.*-softened and uncured "Thiokol"-zinc-oxide mix will not

discolour solvents. After curing, however, there will be an appreciable effect. Apparently at vulcanising temperatures there is an action between D.P.G. and "Thiokol." The reaction product, while present in small amounts, if the D.P.G. is kept to the normal low limits, will give colour to benzol, but practically none to gasoline.

The lower the D.P.G. used, the less the amount of colour obtained. Also, the presence in the compound of materials which neutralise or absorb D.P.G. brings about a reduction in discoloration. - For example, if absorptive carbon black is added to the "Thiokol"-zinc-oxide mix, there will be no colour before cure: slight discoloration of benzol, none of gasoline after cure.

(b) *Thiuram*. Low amounts of Thiuram do not have any effect. Partial replacement of D.P.G. by Thiuram reduces colour.

(c) *Rosin, Pitches, etc.* If the material under consideration gives a coloured solution in a given liquid, a "Thiokol" compound, into which it has been incorporated, will also tend to cause the same kind of discoloration.

2. Rubber. Five-part rubber compounds give the least colour to liquids. Increased rubber in any one type of compound gives more.

3. Pigments. (a) *Carbon Black*. Whereas in rubber compounds black increases solvent discoloration, in "Thiokol" just the opposite is true. This pigment reduces the colour caused by D.P.G. in a cured compound - the greater the black content, the less the colour.

(b) *Gastex* and *Fumonex* stocks give more colour to solvents than a compound with an equal volume of regular carbon black.

(c) *Clay*, *Talc* and *Blanc Fixe* compounds all discolour more than the blacks. Of the three, clay is the best, due perhaps, to its absorptive power.

4. Effect of Cure. Uncured stocks do not discolour unless they contain a soluble rosin. A cure of as little as 20 minutes at 287° F. brings about the colouring in a D.P.G. stock. Increased cures beyond the 20 minutes do not cause a great deal of additional effect.

5. Nature of Liquids. Gasoline shows little colour except in high rubber compounds. Benzol and its related compounds appear worst. The chlorinated solvents are discoloured less than benzol. Duco Thinner colours up very little. Other lacquer thinners vary according to their composition.

6. Temperature of Immersion. The time it takes the colour to show up depends a great deal on the temperature of immersion. Gasoline that will be discoloured to some extent at the end of 24 hours at 158° F. may remain colourless at room temperatures for a year or more.

Curing "Thiokol" to Metals. For some commercial applications it is necessary that a "Thiokol" compound be made to adhere to a metal surface. While no claims are made that "Thiokol" has outstanding properties in this respect, "Thiokol" stocks will be found to have sufficiently good adhesion to warrant consideration for some uses.

The adhesion of "Thiokol" to metal does not appear to be due to any chemical action, but rather

depends on such physical considerations as curing pressure, nature of metal surface, plasticity of compound, etc. An outline of the principle factors that affect the degree of adhesion is presented here to serve as a general guide when a definite problem is under discussion.

General. That the adhesion of "Thiokol" to metal appears to be mechanical in nature and not due to chemical bonding is borne out by the following facts:

a) *Rough or porous metal surfaces* produced by sandblasting or otherwise treating the surface, bring about definitely improved adhesion.

b) *Higher curing pressures* give increased penetration of the stock and better bonds result.

c) *Softness of the uncured compound* gives increased penetration of the stock and improves adhesion.

d) *Greater stiffness of the cured stock* makes for a firmer bond.

e) *Working temperatures.* Heat makes the cured compound slightly softer and consequently weakens the bond.

A compound that gives practically maximum adhesion because of its combination of uncured plasticity and cured stiffness, and at the same time possesses good physical and solvent characteristics, is shown below.

"Thiokol"	100.
D.P.G.	0.10
Thiuram	0.20
Rubber	5.
Zinc Oxide	10.
Carbon Black	25.
	<hr/> 140.30

The Effects of Compounding—Adhesion to Steel.

(a) *Rubber* content does not appreciably affect the adhesion.

(b) *Pigments*. As the amount of carbon black loading in a 5-part rubber compound is increased, adhesion improves slightly until approximately 20 to 25 parts of black are added, then decreases slowly with additional loading.

The lower loaded, softer stocks flow into the metal surface better, but are more easily separated after cure. The more highly loaded compounds do not flow into the irregularities of the steel sheet as readily, but because of the great stiffness of the cured stock, separation is more difficult. It would appear that the maximum point of these two opposing effects is about 20 to 25 of black on 100 of "Thiokol" with 0.10 D.P.G.-0.20 Thiuram plasticizer. More or less softening would obviously require higher or lower pigment loading to attain this maximum adhesion point.

When black is replaced by equivalent volumes of other kinds of pigments, only small differences are obtained in adhesion tests. Pigments which produce softer, more plastic uncured compounds give somewhat better adhesion, but the variation is so slight that for general consideration, carbon black stocks are suggested.

(c) *Plasticizers* do not alter adhesion beyond the effects expected from a change in plasticity.

(d) *Stearic Acid* has a detrimental effect and is, therefore, omitted from formulas when adhesion to metal is the principal consideration.

The Effects of Curing Times and Temperatures.

When the curing temperature is varied through a range from 274° F. to 307° F. and the times adjusted

for these temperature changes, no differences in adhesion are noted.

Increasing the length of time of cure at a fixed temperature produces slightly higher adhesion. This is possibly due to the increasing stiffness of the cured compound at longer cures.

The Effects of Conditions of Processing. (a) *Surface condition* is of extreme importance, just as is true with rubber. The need for cleanliness is obvious.

The surface roughness produced by sandblasting or similar treatments will improve adhesion noticeably, especially in the case of the more highly pigmented compounds.

(b) *High moulding pressures* are desirable to obtain maximum adhesion.

Adhesion to Various Metals. Tests have been run on several metals with the 25-part carbon black compound shown above. The metals were:

1. Sheet Iron.
2. High Carbon Steel.
3. Copper.
4. Brass.
5. Sheet Iron (Copper-plated).
6. Sheet Iron (Brass-plated).
7. Aluminium.
8. Zinc.
9. Lead.
10. Tin.

Sheet iron, high carbon steel, brass, sheet iron brass-plated, zinc, lead and tin showed approximately the same amount of adhesion. Results with aluminium were somewhat poorer. There was no bond to copper, but the union to copper-plated sheet iron was as good as, or better than, to brass-plated.

Effect of "Thiokol" Compounds on Metals. Tests have been run to determine the effect of "Thiokol" when in contact with various metals. The method employed was to place a one-inch diameter disc of several compounds between two plates of each metal and hold them under pressure. Observations were made both at room temperature and at 158° F. The samples were examined to learn whether there was any corrosion or discoloration and to see how much sticking there was to the metal.

The materials used were:

1. Aluminium.
2. Brass.
3. Bronze.
4. Copper.
5. Lead.
6. Sheet Iron — Low Carbon.
7. Spring Steel — High Carbon.
8. Tin.
9. Zinc.

Examination after one Month at 158°F.

Corrosion or Staining. (a) The *copper* sheets were badly discoloured by all the compounds, due to sulphide formation.

(b) *Brass* and *bronze* also show sulphide formation, but not as much as on copper. These samples were both fairly high in copper. Low copper brasses or bronzes are affected less.

(c) *Lead* is only slightly darkened.

(d) *Aluminium, zinc, tin, steel* are not stained.

(e) There was no appreciable difference noted between various "Thiokol" compounds.

Sticking to Metal. (a) Because of the sulphide formation, there was no sticking to *copper*, *bronze* or *brass*.

(b) The softer the cured compound, the more the sticking.

(c) There was less sticking when the pieces were still at 158°F. than after they had cooled.

(d) It is believed that sticking to metals, where there is no corrosion or sulphide formation is primarily a mechanical effect due to flow into the metal surface depressions. The facts, that make this appear so, are that: (1) the softer, easier flowing stock sticks most; (2) sticking is less pronounced, the smoother the metal; (3) at high temperatures, where a given stock is somewhat softer, separation is easier than after the samples have cooled.

Examination after Eight Months at Room Temperature.

(a) *Copper* shows definite sulphide formation at the area of contact.

(b) *Brass* and *bronze* are also discoloured, but much less so than copper.

(c) None of the other metals show any staining.

(d) There is definitely less sticking than in the case of the samples stored at 158°F. and then allowed to cool before testing. This is probably because there is increased flow into the metal surfaces at 158°F.

(e) Raw "Thiokol" and various compounds, either cured or uncured, all show the same staining effects.

Masking of "Thiokol" Odour. The addition of any one of a number of ingredients to a "Thiokol" compound will to some extent mask the characteristic

"Thiokol" odour. While the "Thiokol" will still be noticeable especially at elevated temperatures, such additions have been found to be of sufficient help to warrant their use in a number of applications.

1% or less is usually enough. The small amount does not affect adversely the physical characteristics or swell of the cured compound. Since most of the materials are liquids, it is found that a satisfactory method of milling into the compound is to add them to the carbon black before this pigment is incorporated.

Safrol, methyl salicylate (oil of wintergreen) and Yara Yara are examples of substances that are of interest.

Water Absorption. "Thiokol" is definitely superior to rubber and most other materials in uses where a minimum of water absorption is desired. This characteristic is especially important in electrical applications.

To determine water absorption, sample pieces $3" \times 1"$ and approximately .010 in gauge are cut from laboratory test slabs. Comparisons with rubber, and studies to determine the effects of varying the kind and amount of compounding ingredients have been made by immersing in distilled water at room temperature. With "Thiokol" there appears to be only a surface effect; therefore, the results shown in the following discussion are in grams gain in weight of the test pieces, the areas of which are practically constant. In the case of absorption tests on rubber compounds where the water is probably present throughout the mass, the results are usually expressed in terms of gain on a volume basis.

Raw "Thiokol" takes up practically no water. In one year a $3" \times 1"$ sample having an original weight of

7.229 grams increased to 7.233, a gain of only .004. Generally, with the addition of compounding ingredients water absorption becomes greater. A sample compound containing 100 of "Thiokol," 5 rubber, 10 zinc oxide and 0.25 D.P.G. gained .013 gram during a year. The incorporation of increasing percentages of fillers bring about somewhat higher absorption, as outlined in laboratory tests.

Saflex.

"*Saflex*" is another substitute for raw rubber and is being used at the present time for waterproofing the U.S. Army raincoats and other fabrics.

It is a tough, resilient plastic, which the Monsanto Chemical Co. have made available through a process developed by the Hodgman Rubber Company, Framingham, Mass. Synthetic rosin, treated with solvents for spreading, or taken off in sheets for calendering, may be processed and cured so nearly like rubber that no new equipment, mechanical adjustment, or labour training is necessary. It is said that the American raincoats finished with this product are two pounds lighter than rubber coated ones.

Due to war restrictions, however, it is not possible to give further details of "*Saflex*," and we shall have to await the return of normal times before we can study this synthetic more thoroughly.

Reanite Cements.

There are different methods which are being used for obtaining adhesion of rubber to metal.

The most common is that in which the metal surface is brass-plated, inasmuch as certain rubber

stocks will adhere extremely well to a brass surface of well-defined properties and composition. The procedure is tricky, and during the plating needs very careful control so that the deposited surface is just right, and considerable care is necessary in control of the strength of plating solution, current employed, &c. This method can give excellent adhesion, however, when a suitable rubber is applied to a properly brass-plated metal.

Use has also been made of high pressure applied directly to the assembly, utilising a soft flowing rubber as an intermediate. This can be termed "mechanical adhesion", since it is dependent on forcing a soft rubber stock into the pores of the metal, subsequently vulcanising these veins of rubber in position. The metal surface must be scrupulously clean, and the soft rubber stock is applied directly, followed by the stock which it is desired to stick to the metal. Pressure during cure must be extremely high, since the higher the pressure the better the adhesion, care must be taken to use an accelerator in the stock which will not set up, so that vulcanisation will not take place until the pressure has been exerted for a few seconds.

More recently has come the introduction of certain cements, many of which contain synthetic rosins, rubber derivatives and so forth: Some of these cements make the problem much easier, being less sensitive to slight variation in procedure and conditions, such as are found in any factory. "*Reanite Cements*" are of this type. Previously, most rubber to metal adhesions obtained, used to fall away very rapidly as the service temperature rose. This is true of most cements previously employed as a basis of adhesion. Reanite Cements are capable of giving adhesions of around

1000-lbs. per square inch at room temperature, 300/400 lbs. at 100° C., and 200/300-lbs. at 150° C. Moreover, adhesion is possible with practically every metal in ordinary commercial use, by direct application of an appropriate Reanite Cement to the cleaned metal surface.

Reanite Cements are manufactured by the "*Reanite Corporation*" in Canada, whose sales and development work outside Canada and North America are handled by Monsanto. Reanite products are adequately protected by patents, and Reanite's patent position is supported also by patents for the uses to which the material may be put.

The basis of the Reanite cement is a synthetic rosin let down in suitable solvents, the actual cement having a viscosity about the same as that of a thick rubber solution.

There are several different grades of Reanite, but for most applications, a single cement, namely 120A, is sufficient to give satisfactory adhesion. Tests carried out show that adhesion strength is of the order of 1000-lbs. or more. Reanite will adhere satisfactorily to most metals, including steel, iron, aluminium, lead, brass, &c. By cold application, vulcanised rubber, or latex rubber, can be made to adhere to most hard surfaces. Besides the metals mentioned above, the following materials can be included:- wood, glass, porcelain, synthetic rosins, plastics, concrete and abrasive materials. Likewise, any of these materials can be joined one to the other.

Special attention is drawn to the exceptional bond of aluminium to rubber obtained by Reanite - a field that has not been successfully covered so far by other

methods. Since aluminium is cheaper and lighter than brass or brass-coated metals, there is consequently opened up a wide field for aluminium bonded to rubber by the Reanite process where formerly brass was used.

Reanite is available, therefore, for direct application, to all rubber-to-metal assemblies, and for tank linings, yielding the strongest and cheapest bond of this nature known to industry.

Tests have been carried out using a method similar to that specified by the A. S. T. M. As with all cases of adhesion, scrupulous cleanliness is necessary, otherwise the problem becomes quite hopeless; likewise elimination, wherever possible, of all compounding materials in the rubber stock, liable to bloom, particularly those of an oily, waxy or greasy nature.

Although better adhesion is frequently obtained with relatively lightly compounded rubber stocks, 800-lbs. or more is possible with a stock containing 75% filler. Some of the rubber stocks which have been used are as follows:—

R-100	A	B	C	D
Smoked Sheets	100	100	100	100
Zinc Oxide	10	100	10	50
Soft Black	—		—	15
Whiting	—		40	—
Carbon black	40	3	3	3
Clay	—		75	
Stearic acid	2	2	2	2
Pine tar	3	3	3	3
Flectol-H	1.5	1.5		1.5
Sulphur	3	3	3	3
Ureka	1.25	1.25	1.25	1.25

Cures in all cases have been for 30 minutes at 60-lbs.

The Metal Surface must be Clean. This is best done, either by sand-blasting or pickling. Assuming, therefore, a clean metal surface, one coat of Reanite 120A Cement is applied to the metal and allowed to dry. A solution having been previously made up of one of the above rubber stocks, a similar coat of this rubber solution, mixed with Reanite 120A is then applied over the Reanite. When the surface is dry, the clean rubber surface and metal are assembled, being then ready for cure.

The maximum adhesion is obtained when two or more coats have been used, but for many practical applications one coat of Reanite Cement 120 A is sufficient and provides equal adhesion to that obtainable when several coats of other cements, recently made available to the Trade, are employed.

Results of Tests.

Rubber Stock Used.	Description.	Adhesion—Room Temperature	Lbs/Sq. Inch 100°C
R. 100A	1 coat Reanite 120A	800	520
	1 coat Cement X	800	500
R. 100A	1 coat Reanite 120A	850	580
	1 coat Cement Y	900	620
Cement X = 1 volume 120A and 1 volume cement made from R. 100A.			
Cement Y = 2 volumes cement X plus 1 volume naphtha.			
R. 100B	1 coat Reanite 120A	740	600
	1 coat Cement X	820	600
R. 100B	1 coat Reanite 120A	1000	790
	1 coat Cement Y	1000	640
Cement X = 1 volume 120A and 1 volume cement made from R. 100B.			
Cement Y = 2 volumes cement X plus 1 volume naphtha.			

Rubber Stock Used.	Description.	Abhesion—Room Temperature	Lbs/Sq. Inch 100°C
R. 100C	1 coat Reanite 120A	380	220
	1 coat Cement X	390	250
R. 100C	1 coat Reanite 120A	540	320
	1 coat Cement Y	420	380

Cement X = 1 volume 120A plus 1 volume cement made from R. 100C.

Cement Y = 2 volumes cement X plus 1 volume naphtha.

R. 100D	1 coat Reanite 120A	820	540
	1 coat Cement X	820	540
R. 100D	1 coat Reanite 120A	1000	660
	1 coat Cement Y	1000	640

Cement X = 1 volume 120A plus 1 volume cement made from R. 100D.

Cement Y = 2 volumes cement X plus 1 volume naphtha.

It will be seen, therefore, that for most applications the thinner cement (Y) should be used, made up by combining 120A with a naphtha cement of the rubber stock to be adhered, and subsequent thinning with additional naphtha.

In practically every test employed, the rubber broke and there was no actual separation between the Reanite and metal. From the result given on R. 100C it is quite evident that a cement made from stock high in whiting and clay, has less adhesive properties than one made by the application of the more dilute cement (Y).

The cement should be of fairly low viscosity to obtain the best results, and where heavily compounded stocks are employed, particularly where whiting or clay are used, it may be desirable to employ a lighter compounded stock as the rubber cement.

Ageing. Tests have been carried out to check the ageing of assemblies, and results are as follows:-

Condition of Sample.	Adhesion.	
	in lbs. per sq. inch	
Original	{	1000
		1000
7 days Geer Oven at 70°C	{	1000
		1000
14 days Geer Oven at 70°C	{	1000
		1000
21 days Geer Oven at 70°C	{	1000
		1000
5 hours air bomb at 125°C	{	860
		1000

It is quite evident, therefore, that the Reanite bond withstands ageing very satisfactorily.

Tests in Oil and Naphtha. Samples were immersed for 24 hours before testing. Results as follows:—

	Adhesion.	
	in lbs. per sq. inch	
Lubricating Oil	{	920
		1000
Naphtha	{	80
		80

Although there was considerable swelling of the rubber in both cases, *Reanite* obviously resists the effects of lubricating oil, but is seriously affected by Naphtha. This resistance of *Reanite* to motor oil has been further checked by placing an assembly made up by adhering a stock consisting of

Smoked sheets	80
Zinc oxide	5
Soft black	60

Glue master batch	20
<i>Flectol-H</i>	2
Sulphur	2.5
<i>Ureka White</i>	1.125

to polished aluminium alloy and placing in motor oil, subsequently examining after 14 days. The adhesion after this time was excellent, and immersion appeared to have had no effect although the rubber sample had increased in gauge 0.275" to 0.303".

The adhesion problem to "Neoprene" and "*Thiokol*" says Monsanto is still being investigated, although encouraging results have been obtained by a modification of the above procedure.

Advantages of Using Reanite. In press cure the assembly can be removed from the moulds whilst still hot, without in any way tearing the rubber loose from the metal. This is not normally possible when other cements are used, as the adhesion is seriously impaired and it becomes necessary to cool down the article before removal. Where desirable, cures can be effected in open steam, in talcum, or hot air, without any appreciable reduction in the adhesion.

Reanite cements can be stored without danger of decomposition. Before use, it is very desirable to give the solution a thorough stir.

As illustrated above, the *Reanite* bond withstands high temperatures. Where required the bond can be made to stand 300° F and still be stronger than the 200-lb. per sq. inch requirement common to normal commercial practice.

Use can also be made of *Reanite Cements* for direct bonding of vulcanised rubber to metal and other hard surfaces, at room temperature, provided a period of three to four days is allowed before the assembly

is subjected to severe strain. In such cases, the surfaces are cleaned free from oxide and grease, and a coat of Reanite 120A is applied to the metal. The rubber is equally coated with a cement, half Reanite 120A and half rubber solution. When tacky, the two surfaces are joined, and preferably left under weights. Fair adhesion results.

Reanite Cements are simple to use, and may be applied either by spraying, brushing or dipping. In connection with the use of a spray-gun it is important that the cement should not dry before it reaches the surface to be sprayed; therefore the spray-gun should not be held too far away. Using 20lbs. air pressure and with a cheap type spray-gun, the nozzle should be held at a distance of about four inches.

The Monsanto Chemicals have a fairly extensive programme on hand with all synthetic rubbers. They are experimenting with Buna S, Chemigum, Hycar TT synthetics, which are suitable for replacing rubber in tyres, tubes etc. They are also experimenting with oil resisting variety of synthetic rubbers, namely Hycar OR, Perbunan and Thiokol RD, which are designed for use in technical applications requiring oil and solvent resisting properties.

The Monsanto's accelerator "*Santocure*", full details of which appear in Chapter II, is proving to be of considerable interest in synthetic rubber compounding, showing up very much more satisfactorily than Thiotax and Thiofide. As already stated, "*Santocure*" is chemically Cyclohexylamine benzo-thiazyl, and possesses a very high degree of delayed action, which is invaluable in compounding synthetic rubbers, as excessive heat develops during their

processing. When the vulcanisation commences, this proceeds very rapidly and the curing curve is very steep and ends up with the desirable flat curing plateau-effect as obtained by the Thiazole types, as our own experience with the Ureka types clearly shows.

The American War Production Board also released in 1942 a programme* for the production of synthetic rubber using farm products to secure grain alcohol as a source of butadiene, and in the same year the Secretary of the Department of Agriculture, Washington, in a statement before the U. S. A. Senate Committee on Agriculture and Forestry Investigating Uses of Farm Crops in production of Alcohol and Synthetic Rubber, said, in part: "I believe" "that the use of part of our reserve stocks of corn and" "wheat as material for butadiene offers the best pos-" "sibility of greatly increasing our production of synthetic" "rubber as early as next year." Large stocks of corn and wheat are available and the process of converting 95% alcohol to butadiene was technically established. He stated that considerable expansion of facilities for making alcohol out of grain is possible in America's existing distilling plants with the use of relatively small amounts of copper and steel, and indicated that if such plants were converted to high-proof production, 200,000,000 gallons of alcohol for making butadiene could be produced after allowing for production of alcohol for other war purposes. The 80,000,000 bushels of wheat or corn required would produce 222,000 tons of butadiene for conversion to approximately 240,000 tons of buna-type synthetic rubber.

The question arises whether the alcohol process will require more copper and other scarce materials

than any other process? In fact the chemical branch of the W. P. B. is reportedly opposed to the alcohol-butadiene programme on the ground ~~that it would require large tonnages of strategic materials and that butadiene is more cheaply produced from petroleum products.~~ The following composition of strategic metals for alcohol butadiene and petroleum butadiene per 1000 tons of butadiene was presented to the said Committee:—

	For Alcohol process.	For Petroleum process.
	Tons	Tons
Copper	50.60	9.00
Nickel	1.00	2.05
Chrome Metal	2.20	5.00
Steel Plates	140.00	165 to 194.00

Other methods for producing synthetic rubbers are under investigation in America and are ample proofs of the immense utility that synthetic products can be to mankind.

Neoprene.

"*Neoprene*" is a synthetic rubber supplied by the Imperial Chemical Industries, and to popularise the product, I. C. I., are publishing a magazine called the "*Neoprene News*", which gives interesting and valuable information to those interested in the use of this synthetic, for it is said that Neoprene can be used to make every kind of article so far made of natural rubber.

The main object of "*Neoprene News*" is to demonstrate that Neoprene is to be preferred to raw rubber. The I. C. I. claim that one Neoprene part outlasts several rubber parts, concluding therefrom that one pound of Neoprene is equivalent to many

pounds of natural rubber and that consequently, Neoprene is cheaper than raw rubber. They also declare that their product is fireproof, whereas rubber....? These are strong assertions, and the question arises whether synthetic rubber in general, and Neoprene in particular, will be used instead of raw rubber, and whether the rubber manufacturer will not be able to find out other ways to use the natural product? It is a fact that in some cases synthetic rubber is superior to raw rubber, especially that product which resists oils, petrol and direct sunlight, and that it can be used where natural rubber has failed.

It may be that an article made of raw rubber which may resist wear and tear for say three years, will resist five years if made of Neoprene. But the "*Neoprene News*" itself admits that five years are needed to prove such an assertion! The claim that rubber is inflammable certainly should not condemn its value and usefulness. Petrol is inflammable, wood is combustible, but their value and usefulness are recognised the world over. Is Neoprene really flame-proof? Certainly we agree with the "*Neoprene News*" that a fan should be covered with Neoprene when the said fan's function is to exhaust acid fumes containing sulphuric-acid-mist, sulphur dioxide, sulphur trioxide and steam; we agree that suits, aprons and gloves can be made of Neoprene, just as they can be produced from natural rubber; we agree that Neoprene which will remain "*new*" much longer than rubber articles of the same kind, even though the Neoprene articles may be similar, in appearance and mechanical properties, to the rubber goods; we agree that Neoprene-compounds are superior to rubber-compounds in that the former offers increased resistance to heat, light, ageing, water absorption and also to the deleterious effects due to

exposure to oils, solvents, greases and oxidising agents, such as ozone and other numerous chemicals.

But would the "*Neoprene News*" agree with us, when we affirm that, so far as the insulation of electrical cables and wires is concerned, Synthetic rubber, so far known alone would be absolutely useless?

We are pleased to learn that such a new material as Neoprene which belongs to the same general chemical group as rubber, and which, in its raw state, has the same physical properties as rubber, has been discovered. We hope that Neoprene, like other Synthetic rubbers, will endeavour to establish and maintain friendly relations with natural rubber, so that both the natural product, and the Synthetic material, may be used in the same rubber article, for the benefit of the Rubber Industry in general, and the rubber planter in particular.

It is, however, too much to expect the synthetic to replace the natural!

There was a time when "*ebonite*" was suggested as a substitute, in some cases, for copper. About thirty years ago, when I was the Manager of an important Rubber Factory in Belgium, a certain paper manufacturer became alarmed, because his copper installation was being eaten up by the muriatic acid, which was used to decompose the waste with which he was making his paper paste. "*Why not replace all your pipes, couplings, tapes, funnels, in a word the whole copper installation, with ebonite!*" was my suggestion. In accordance with my advice the paper manufacturer had all the copper replaced by ebonite, and the modified installation gave him full satisfaction. Did that mean that ebonite replaced copper? In that

particular case, it certainly did, but such a replacement is certainly not necessary or advisable in all cases.

Neoprene, Thiokol and other synthetic rubbers will probably share this experience in their relation to rubber. Synthetic and natural rubber will not destroy each other, but will combine their properties for the benefit of the rubber industry. I.C.I. realise this, and in one of their reports, suggest "*the bonding of rubber to wood with the help of Neoprene*"!

The I.C.I. are not only publishing the "*Neoprene News*", but are also issuing periodical Reports relating to their synthetic rubber. We give numerous extracts from these periodicals.

First let us consider the chemical composition of Neoprene. The I.C.I. explain that it is a polymerised form of Chloroprene, obtained from coal and limestone, which are made to pass through a number of chemical processes to obtain the said product.

There are already various Neoprene types: The types E, G, G N, Z, I and M. Due to war conditions, the I.C.I. are unable to supply them all, and often one type must necessarily be replaced by another. Such replacements, however, are not easy and necessitate altering the formula, as well as the curing conditions. In this respect three types of Neoprene have to be considered. These are types E, G, and M, and the points to be dealt with are the modifications necessary when changing from type E to type G and vice versa, The case of type M, state the I.C.I., is relatively simple, since it consists merely of type E, in which the usual anti-oxidant is replaced by a non-staining anti-oxidant.

The following table summarises the differences in processing requirements that exist between these three types of Neoprene.

	Neoprene Types E & M	Neoprene Type G
Zinc oxide	10% on neoprene.	5% on neoprene.
Light calcinated magnesia	10% „ „	4-7% „ „
Wood rosin	5% „ „	Omit.
Sulphur	Can be used if desired.	Omit. ⁽¹⁾
Softeners (cotton- seed oil, light mineral oil, or pine tar)	More than in type G mixes.	Less than in type E mixes.
Tack producers (Cereclor I)	Needed for “building up” operations,	Not needed.
Detackifiers (paraffin wax or oleic acid)	Not generally needed for calendering or extrusion.	Needed for calendering or extrusion. Do not exceed 2% with paraffin wax: up to 5% of oleic acid can be used.
Thioplasts	Can be added if required with- out difficulty.	When 20% or more is to be added special care is needed.
Factices	Can be used with- out difficulty.	Can be used without difficulty.
Value for bonding to metal.	Good. Sulphur should be added	Slightly better than type E. Sulphur should preferably be added.
Curing conditions	60 minutes at 40 lbs. of steam.	30 minutes at 40 lbs of steam. · MBTS (not exceeding 2%) will correct any tendency to scorch.

(1) In mixes for bonding to metal, a little sulphur may advantageously be present.

Type E, which was the first Neoprene supplied to the Industry, has the following basic formula:-

Neoprene Type E	100	parts by weight.
Light Calcinated Magnesia	10	„ „
Wood Rosin	5	„ „
Zinc Oxide	10	„ „

The magnesia and wood rosin should be added together and the zinc oxide last. The mill must be kept cool, avoiding the slight degree of warmth prescribed for working type G mixes. A type E compound tends to show less tackiness than a compound type G. Calendering and extrusion operations thus tend to be simpler, but where good building-up properties are necessary, a tack-producing agent like Cereclor I, in quantity up to 5% on the weight of Neoprene, may have to be added in order to obtain the effects secured with type G. In fact, type E mixes need more softener than type G mixes for comparable properties and effects, and Neoprene type E cures more slowly than type G. The usual time is 60 minutes instead of 30 minutes at 40 lbs. steam pressure, or the equivalent at other curing temperatures.

Type G is the odourless variety of Neoprene, the basic compound of which is

Neoprene Type G	100
Light Calcinated Magnesia	4
Zinc Oxide	5

The zinc oxide should not exceed 5 parts by weight, but the magnesia may be increased on occasions to 7 with advantage. Zinc oxide should be added last as in the case of type E. When mixing type G compounds, it is recommended to run the mill slightly

warm. Generally less softener is used with type G than with type E, but the type of softener is the same, i. e. cotton seed oil, light mineral oil, or pine tar. It should be noted that with type G some calendering and extruding difficulties may occur unless a tack-reducing agent is added. A 2% of paraffin wax serves this purpose. But should such a quantity fail to reduce the tackiness to the desired extent, oleic acid may be used instead, as it is of similar efficacy, weight for weight, and can be added in larger amounts, say up to 5%.

Type G compounds cure twice as rapidly as type E compounds. The curing conditions given are usually 30 minutes at 40 lbs. of steam. It is also to be noted that if difficulties are encountered with type G due to scorching or jelling of solution, they may be overcome by the addition of 1% of Vulcafor MBTS on the weight of Neoprene, and there is no effect on the time of heating required for a full cure and no loss in ultimate tensile strength or resilience.

Type M is a non-staining type. Light coloured stocks show very much less discolouration on exposure than in the case of the two aforesaid types, and similarly discolouration of petrol, or other solvents, that come in contact with the cured stock is reduced to a negligible degree. Neoprene Type M is used only where such non-staining characteristics are required. In all other respects, its properties are identical with those of Neoprene Type E, with the result that in any mix, or process in which type E is normally employed, type M may be adopted without making any change whatsoever, except that when type G is to be used for any purpose demanding non-staining characteristics,

the compounding ingredients to be added, should be so selected that they will not detract from these non-staining properties.

Type GN is a new, improved, unplasticised type of Neoprene which must be plasticised on the ordinary rubber mill prior to, or in conjunction with, the mixing and compounding operations. When vulcanised, type GN compositions possess all the desirable properties of Neoprene type G, and in many respects are superior. Thus, because type GN contains only non-discolouring stabilisers, it gives, coloured or white stocks, which not only have an excellent appearance, when freshly made, but in addition, retain their original appearance remarkably well on exposure to bright sunlight. Type GN, like type G, is substantially odourless. After type GN has been plasticised to the same degree as type G, it behaves in a very similar way during the subsequent compounding. No storage difficulties are likely to be encountered as unplasticised Neoprene Type GN is as stable at room temperatures as Neoprene Type E and is only slightly less stable after being plasticised. Guanidines, and particularly Vulcafor DOTG, are excellent chemical plasticisers for Neoprene type GN. Only about 0.5% of DOTG is needed for most purposes, but the amount may be increased up to 2% when very soft stocks are required. For adding the Vulcafor DOTG, the following procedure is recommended, and the intimate mixture of the formula given below is made up by tumbling the ingredients in a closed container.

Whiting	75	parts by weight.
Vulcafor DOTG	20	" "
Stearic Acid	5	" "

This mixture is added directly to the Neoprene type GN immediately the batter starts to run on the mill which should be maintained at a temperature of between 40 and 60° C. In this way an even dispersion of the plasticiser is obtained without the formation of adhesive patches on the mixing rolls. The stearic acid functions as a lubricant and is a useful compounding agent, as in type G. About 5 minutes' milling is usually sufficient, but for large scale batches as long as 15 minutes may be necessary. It should be noted that Vulcafor DOTG has a further delayed plasticising action, and storage for 24 hours gives a slight increase in plasticity.

The following is a basic formula for Neoprene type GN stocks:—

Neoprene type GN	100	parts by weight.
Vulcafor DOTG	0.5 to 1.0	„ „
Stearic Acid	0.25	„ „
Nonox S	2	
Light calcinated magnesia		4	„
Zinc Oxide	1	„

Cure: 30 minutes at 141° C.

The order of mixing is the same as for all Neoprenes and it should be noted that type GN resembles type G in that no wood rosin is required. The zinc oxide requirements are however, considerably smaller, although the zinc oxide can be raised to 10 parts where an increase in heat resistance is required.

The following is a typical Neoprene GN mix containing a semi-reinforcing carbon black.

Neoprene Type GN	100	parts by weight.
Vulcafor DOTG	0.5 to 1.0	„ „
Stearic Acid	0.25	„ „

Nonox S	2	parts by weight.
Light calcinated magnesia			4	" "
SB 1 Carbon Black		28.8	" "
Zinc Oxide	1	" "

Cures at 141° C.	Modulus (kgs/Cm ²)		Tensile strength (kgs/Cm ²)	Elongation %	Hardness (Shore).
	300%	500%			
7½ minutes	23	60	144	1010	41
15 "	67	135	216	800	55
30 "	83	163	212	700	57
60 "	86	174	206	600	58

Neoprene Type GN may be plasticised and compounded either on open mills or in Banbury mixers. When plasticising on open mills, it is preferable to use a warm mill with the rolls set fairly close. After two passes through the mill, the Neoprene Type GN will resemble a tough sheet of rubber. At this point the plasticiser should be added, care being taken to distribute it as uniformly as possible throughout the batch. After milling for approximately 5 minutes, the Neoprene will soften and start to run smoothly, so that after a total of 8 to 10 minutes' milling, it will be plastic and ready for the additional compounding ingredients.

A typical open mill mixing schedule for Type GN is:

Data: Mill, 60 inch.

Roll temperature, 40—55° C.

Recommended friction ratio, 1/1.15—1.20 which is the normal speed mill.

Batch size, based on batch containing 40—60 lbs. neoprene.

Mixing: Start with tight mill rolls so as to produce $\frac{1}{8}$ inch gauge sheet.

Approximate Time in Minutes.

- 0 Add neoprene Type GN. After 3—4 passes through mill, sheet will form.
- 2 Carefully add Vulcafor DOTG to mix by passing sheet through mill and cut back.
- 10 Add factice if used. Add modifying agents (anti-oxidants and retarders) and magnesia.
- 14 Add black, clay and other dry fillers and softeners. (Best practice is to add dry fillers to mix in small increments, followed by softeners. This practice prevents softeners from breaking through batch and exposing front roll. Continue small additions alternately until all fillers and softeners are worked in. If batch is too large, it is good practice to make 'cut outs' from the ends of the roll and reduce the size of the mix). When dry fillers and softeners are incorporated, cut off enough stock to obtain a small rolling mix.
- 29 Add zinc oxide.
- 32 Add 'cut out' and cut 5 to 7 times to blend.
- 36 Start batching off.
- 39 Batch off.

When the mixed stock is to be stored for any length of time before further processing, it is recommended that the zinc oxide and accelerator be omitted and added on the warm-up mill.

When mixing on an open mill, the ingredients should be added as rapidly as possible since the shortest possible milling time usually gives the best result.

Type Z is a new oil-resistant synthetic rubber of the chloroprene class and has a greater resistance to swelling in oils and solvents than other types of Neoprene. It has been suggested by the I. C. I. primarily to meet certain very stringent specifications for materials having approximately zero swelling in oil, but it is manufactured only in limited amounts. The compounding of Neoprene Type Z follows closely the lines already laid down for Type E. Carbon Black, for Type Z, is a valuable compounding ingredient. Channel Blacks, such as Kosmos T, give reinforcement, while Soft Blacks act as non-reinforcing fillers. Lamp Black is particularly useful when hard stocks of high resilience are required, but Soft Blacks give superior heat resistance. Sulphur, although not a necessary ingredient for vulcanisation, is even more valuable for tightening up cure than in Type E, and from 1 to 2 parts of it on 100 parts of Neoprene Type Z is recommended in all cases, except when heat resistance is of primary importance.

I. C. I. recommend the addition of at least 2% of an anti-oxidant such as the Neozone A, Neozone D or Nonox S. For maximum heat resistance, the usual mixed anti-oxidants Neozone D and Nonox NSN, or Nonox S, and CC should be added in a concentration of 2% each.

Pine tar, tricresyl phosphate, dibutyl phthalate and cumar gum rosin are valuable tack-producing softeners, and partial replacement of wood rosin by twice the weight of pine tar is often advantageous. The curing characteristics of Neoprene Type Z are similar to those of Neoprene Type E, and the same type of plateau on the overcure is obtained. For technical cures, 30 minutes at 60 lbs. in steam pressure is recommended.

The following are two typical formulas together with the physical properties of the vulcanisates:-

Mix No.		ZN 122.	ZN 142.
Neoprene type Z	100	100
Light calcinated magnesia		10	10
Wood Rosin	2	5
Pine Tar	8	10
Nonox S	2	2
Kosmos T	35	—
Lamp Black	—	110
Trigresyl Phosphate	—	5
Sulphur	1	2
Zinc Oxide	5	5
Cure at 60 lbs. steam pressure		30 minutes	30 minutes
Hardness (Shore)	64	81
Tensile Strength (Kg. per sq. cm.)		262	137
% Elongation at break	731	279
Resilience* (% at 50° C.)		60	—

Neoprene Type I is another new oil-resistant synthetic rubber of the chloroprene type. It resembles Neoprene type Z in its resistance to swelling by oils, and swells to a considerably smaller extent than do types E, G, and GN. The specific gravity of Neoprene type I is 1.21. Uncompounded Neoprene type I is slightly more plastic than type Z and the vulcanisates obtained from it are harder and slightly less resilient than those obtained from an equally loaded compound based on type Z.

Neoprene type I is compounded and vulcanised in exactly the same way as type Z and the flat curing characteristics of other Neoprene types are maintained. Both the Neoprene types I and Z are interchangeable

for all oil-resisting applications, provided that slight alterations are made in compounding formulas to correct for the slightly increased hardness of type I.

In storage properties, Neoprene type I is also very similar to type Z. The results of tests indicate that the material can be stored up to at least six months under good factory conditions.

The essential vulcanising ingredients are similar to those used with Neoprene type E, and the following is the basic mix as suggested by the I. C. I.:-

Neoprene type I	100.
Light calcinated magnesia		10.
Wood Rosin	...	5.
Zinc Oxide	5.

Carbon Black is an especially valuable compounding ingredient for type I; Channel Blacks, such as Kosmos T, give reinforcement, while Soft Blacks, such as Thermatomic Black, act as non-reinforcing fillers. Lamp Black is particularly recommended for hard stocks having resilience, but Soft Blacks give superior heat resistance. Mixed anti-oxidants, such as two parts each of Nonox NSN and Neozone D, or Nonox CC and Nonox S are of special interest for high temperature resistance, while the zinc oxide should be increased from five to ten or fifteen parts on a hundred parts of Neoprene type I. Sulphur should, of course, be omitted from stocks designed to work at high temperatures. Owing to the high oil resistance of Neoprene type I, the range of permissible softeners is more limited than in the case of Neoprene types E, G, or GN, and oil materials should only be used in limited amounts. Pine tar, tricresyl phosphate, dibutyl phthalate, balata rosin, and cumar gum are particularly recommended for that purpose. The addition of 2%

anti-oxidant is suggested in all cases except for heat resistant stocks, which have already been discussed, but Nonox S is especially valuable as it has a pronounced softening action.

Sheets of Neoprene type I, like type Z, when taken off the mill, should always be dipped into water or sprayed before stacking. When compounds of type I are to be stored, the zinc oxide should be omitted and added only to the compound on the warming-up mill. The vulcanisation characteristics of Neoprene type I resemble those of Neoprene type Z very closely. A curing range of from 40 to 80 minutes at 141°C. is recommended.

The following are typical compounds. Mix No. 57 is a soft compound with a minimum loading. Mix No. 122 is a medium-hard compound with excellent tear resistance and good all-round physical properties. Mixes Nos. 142 and 200 are hard gasket stocks, the latter with good physical properties at low temperatures.

	57	122	142	200
Neoprene type I	100	100	100	100
Light calcinated magnesia	10	10	10	10
Wood Rosin	5	2	5	5
Pine Tar	—	8	10	—
Dibutyl Phthalate	—	—	—	25
Nonox S	—	2	2	2
Kosmos T	—	35	—	15
Lamp Black	—	—	110	110
Tricresyl phosphate	—	—	5	—
Soft Carbon Black	15	—	—	—
Sulphur	—	1	2	2
Zinc Oxide	5	5	5	5

Cure: 80 minutes at 141°C.

Synthetic Extruding Stocks should be made of the Neoprene types E, G, or GN. The special requirements of a synthetic extruding compound are softness at extruding temperatures, good lubrication and freedom from scorching. A combination of these three factors gives a high-speed extruding mix. Softness or plasticity should, however, be controlled to prevent the flattening of the extruded article during cure.

Suitable compounding ingredients are soft blacks, whiting and dark factice. The chief lubricants are paraffin wax and stearic acid.

As an indication, we give below a few formulas as suggested by the I. C. I.

With Neoprene Type E

	G. 3671	G. 3672	G. 3673	G. 3674	G. 3676
Neoprene type E	100	100	100	100	100
Dark factice	20	20	20	10	40
Light calcinated magnesia	10	10	10	10	10
Thermatomic black	70	110	150	190	175
Wood rosin	5	5	5	5	5
Mineral oil	5	5	5	5	10
Neozone D	2	2	2	2	2
Nonox NSN	2	2	2	2	2
Sulphur	1	1	1	1	1
Paraffin wax	0.5	0.5	0.5	0.5	—
Zinc oxide	10	10	10	10	5

Cure: 60 minutes at 141° C.

With Neoprene Type G

	G. 3677	G. 3678	G. 3679	G. 3680	G. 3681
Neoprene type G	100	100	100	100	100
Dark factice	20	20	20	10	25
Light calcinated magnesia	4	4	4	4	4
Thermatomic black	70	110	150	190	
Mineral oil	5	5	5	5	10

	G. 3677	G. 3678	G. 3679	G. 3680	G. 3681
Neozone D	2	2	2	2	2
Nonox NSN	2	2	2	2	—
Paraffin wax	0.5	0.5	0.5	0.5	—
Vulcafor MBTS	1	1	1	1	—
Zinc oxide	5	5	5	5	5
Pine tar	—	—	—	—	5
Kosmos T	—	—	—	—	40
Black S. B. 1	—	—	—	—	50

Cure: 30 minutes at 141°C.

With Neoprene Type GN.

	G. 3683	G. 3684	G. 3685	G. 3686	G. 3687
Neoprene Type GN	100	100	100	100	100
G 810*	—	1.0	2.5	2.5	—
Dark Factice	20	20	20	10	20
Light calcinated magnesia	4	4	4	4	4
Thermatomic Black	70	110	150	190	175
Mineral Oil	5	5	5	5	—
Tricresyl Phosphate	—	—	—	—	10
Neozone D	2	2	2	2	2
Nonox NSN	2	2	2	2	2
Vulcafor MBTS	0.5	0.5	1	1	1
Paraffin Wax	0.5	0.5	0.5	0.5	1
Zinc Oxide	5	5	5	5	5

Cure: 30 minutes at 141°C.

Self-curing Cements based on Neoprene Type E and Type GN are as follows:-

	A.	B.
1. Neoprene Type E (Plasticised)	100 parts	100 parts
Triethanolamine	0.75 „	— „
Wood Rosin	—	5 „
Catechol	—	2 „

G 810 is the plasticiser for Neoprene Type GN.

			A.	B.
Salicylic Acid	— parts	2 parts
Zinc Oxide	5 "	— "
2. Neoprene Type GN (plasticised*)			100 parts	100 parts
Triethanolamine	0.75 "	— "
Zinc Oxide	5 "	— "
Catechol	— "	2 "
Salicylic Acid	— "	4 "

Mixes A and B are prepared on the mill in the usual manner and then dissolved separately in three times the weight of benzene. These 25% stock-solutions can be kept for an indefinite period at normal temperature, but on mixing them together in equal parts, they give a cement with powerful self-curing characteristics. At room temperature, their properties are as follows: A film, after evaporation of the solvent, is found to be fully cured after 48 hours, and both the cements gel in about 24 hours. Cure is judged by complete insolubility of the film in toluene.

The I. C. I. have recommended the *Neoprene Latex No. 57*, which is an aqueous dispersion of very fine negatively charged particles of partly cured Neoprene. The latex contains 50% of solid Neoprene and has the following properties:-

It is very stable to agitation and to the addition of compounding ingredients. The films obtained from this latex are perfectly clear. Type 57 films can be cured at low temperatures, provided sufficient time is allowed. Films of normal thickness cure within 15 minutes at 140°C. or in one hour at 120°C.

* Neoprene Type E and Type GN are plasticised either by cold milling for 15 minutes, or by 5 minutes treatment on a warm mill with the addition of 0.5% Vulcafor DOTG.

Compounding with sulphur, zinc oxide and certain accelerators favourably affects the cure of Type 57 film and gives still further improved physical properties.

Neoprene Latex Type 57 may be used for the following purposes:-

- (a) fabrication of balloons, by dip process, of remarkably fine ageing properties for meteorological use;
- (b) preparing thin film articles by dip process;
- (c) preparing oil-resistant and heat-resistant spreadings and cable tape;
- (d) preparing cements for bonding together leather scrap, paper pulp and other materials in the manufacture of artificial leather or water-resistant boards;
- (e) impregnating textile fibres for the manufacture of ropes, beltings etc.

Neoprene Latex No. 57 can replace, to a certain extent, natural rubber latex for producing goods with improved resistance to oil, grease and heat.

Neozone D as an anti-oxidant for Neoprene Latex No. 57. The use of this anti-oxidant is strongly recommended as a protection to Neoprene-Latex-Composition against deterioration under severe service conditions, and where a maximum resistance to oxidation and heat is required.

The quantity of Neozone D recommended is 1 part weight per 100 parts wet weight of Neoprene Latex Type 57. It is necessary to add the Neozone D in the form of an aqueous dispersion. This dispersion may conveniently be prepared by grinding, for 24 hours, in a ball or pebble mill, a paste of the following composition:-

Neozone D	100	parts	by weight
10% Casein solution	30	„	„
Disperol L N	1	„	„
Distilled water	69	„	„

The casein solution may be prepared by wetting 10 parts weight of casein with 87 parts of distilled water, adding 1 part of concentrated ammonia solution and then heating, whilst stirring, to a temperature of about 70° C. until a homogeneous solution is secured. After cooling, 2 parts weight of a 10% solution of sodium trichlorophenate should be added as a preservative.

Bonding Rubber to Wood.

Rubber is now widely used for constructional work, and enters into an extensive range of composite articles. It is not only used in contact with metal, but is even used in contact with wood.

Bonding rubber to wood, states the *Imperial Chemical Industries*, in one of their reports on the subject, is by no means easy, and they have succeeded in developing a sound method.

This method involves the use of "*Chlorinated rubber*"* in combination with Neoprene interlayers and shows how the latter product is assisting the rubber manufacturer over and above supplying him with a new raw material on which to base his compounds. The bonding process was originally developed for use with the rubber tread given below, but is equally applicable to a wide range of other compounds:-

A.	Rubber Tread Stock.	Parts by weight.
	Smoked Sheets 100
	Zinc Oxide 5

*See page 89 chapter V.

Rubber Tread Stock.		Parts by weight
Kosmos T	40
Vulcatax CH	...	2
Sulphur	3.5
Vulcafor MBT	...	0.75
B. Alloprene Mixture.		
		Parts by weight
Chlorinated rubber	...	30
Red Lead	10
Toluene	100
C. Neoprene Stock.		Parts by weight.
Neoprene Type G	100
Light calcinated magnesia		10
Thermatomic carbon black		50
Cotton seed oil	5
Nonox NS	2
Zinc Oxide	2

The rubber and Neoprene stocks are made on the mill in the usual manner.

The surface of the wood is painted with the Alloprene solution, allowed to dry, and a second coat applied and also allowed to dry. Then a very thin sheet of the neoprene stock is pressed firmly in contact with the Alloprene-red-lead coating. The uncured rubber stock is next applied to the Neoprene layer and the work finally cured under steam pressure for 45 minutes at 141° C. This gives, state the I. C. I., a first class bonding to wood.

Tyres.

Owing to the present scarcity of natural rubber, a large number of the tyres, now in use, is made from Synthetic Rubber. At first the rubber part of the mix, for the fabrication of such tyres, was composed of 50% natural rubber and 50% Synthetic Rubber. At present,

however, even as much as 98% of the mix is synthetic rubber.

Is this proof that tyres made solely from synthetic rubber are better than those made from raw rubber?

For a suitable reply to such a question, it is necessary to refer to the tyre thermometer, which reveals that the synthetic rubber tyre normally runs a temperature of 210° F. on the road, whereas the temperature attained by a natural rubber tyre, running under the same conditions, is only 180° F.

The difference between the running temperatures of synthetic rubber tyres, and those made from natural rubber, is of great importance, for the heat caused by the flexing of the tyre, as it rotates on the road, tends to destroy the natural rubber, whereas it does not affect the synthetic rubber.

But tyres are not made from natural or synthetic rubber alone! They are built on canvas, and the critical temperature at which the deterioration of the cotton starts is 230° F.

Until, therefore, some means, or methods, to reduce the heat generated in synthetic rubber tyres, running at high speed are found, it will be safer to run on natural rubber tyres, which do not generate the heat capable of causing the blow outs of the tyres.

An important step towards the development of synthetic rubber closely approximating natural rubber, therefore, will be the discovery of a special type of synthetic rubber which, under running conditions, will generate less heat and thus permit its use in the manufacture of heavy truck tyres, 60% of which, in spite of its scarcity, are still made from natural rubber.

CHAPTER X.

Fabrication of Rubber Goods.

AS an introduction to this chapter, it would be well, first of all, to consider the important question of "*uniform curing conditions*" required for obtaining perfect vulcanised articles.

In most of the factories, ordinary pressure gauges are employed to control the important factor of vulcanisation, but it would seem that sufficient attention is not paid to that little inoffensive-looking instrument, which is surely one of the main causes of trouble, in the Rubber Factory.

In the first place, it may be stated that pressure gauges are notoriously inaccurate. They are subject to considerable changes from ordinary usage, and if subject to rough usage, or sudden application of excess pressure, their inaccuracy is almost beyond computation.

The engineer, or even the aspirant technical man, at once appreciates, of course, that pressure, whether it be by steam, hot water, or air, does not in any way bring about vulcanisation, which is only effected by temperature. Unfortunately, it is generally assumed that the well established steam-pressure-laws for satur-

ated water vapours always apply to ordinary plant operations. This is rarely true, because actual plant steam invariably contains a certain amount of air, so the only safe method of measuring temperature, for rubber work, is by the use of a thermometer. The ordinary direct reading mercury thermometer, on the vulcaniser, is the best, but the remote indicating, or recording thermometer, whether of the mercury type, or steam pressure type, is almost equally good, and both are indeed far superior to the pressure gauge. The well established rule of all technical men, when unknown difficulties occur in vulcanisation, is first to check the supposed temperature at which the cure was presumed to have taken place. In about 95% of the cases investigated, the trouble is located in the vulcaniser. Those having had less experience in this line can well profit from that of others.

In volume I various methods for producing Bicycle Tyres and Tubes, Sheetings, Rubber Hoses, Moulded and Dipped Goods, Rubberised Fabrics are described....

The manufacture of rubber articles is rather complicated. Most of the items are partially made by hand, then vulcanised, either in open steam, or in the press, wrapped with cotton, or in moulds, as the case may be. For obtaining satisfactory results, one needs not only skilled hands, but accurate moulds and up-to-date machines of precision, such as good Calenders capable of sheeting rubber at specified thickness; Rubberising Machines capable of proofing fabrics, so that the weight of the applied solution is as stipulated in the specification; Forcing Machines, with feeding and talcum devices, capable of extruding ebonite, in rods and tubes, with a variation in diameter of not more than 0.05 of a m.m., when the tubes or rods are

supplied polished, and not more than 0.25 to 0.75 m.m., when they are supplied unpolished, i. e. just as they are extruded from the Forcing Machine.

Even the production of moulded goods is not a small affair, for it is not enough to have the mould of the correct size to produce a perfect article, the mixing of the compounds, and the time of vulcanisation, being two factors of importance, which dare not to be overlooked.

Contrary to what one may imagine, the biggest rubber article is not the most difficult to produce, and we agree with the reply given by the Manager of a certain Rubber Factory, who employs more than 5000 hands, daily produces a large number of tyres and tubes, tons of rubber sheetings, and hundreds of feet of various rubber hoses, when he was asked, what, in his factory, was the most delicate job? He answered **"Piston Cups for hydraulic brakes on motor cars"**, and explained that, if a cup was wrong, the brake would not work, and that there may be sudden death!

Piston Cups for hydraulic brakes! Is more skill needed to manufacture these than the fabrication of a motor tyre? One would hardly believe it, but it is a fact! A piston cup is not even 3 m.m. thick, with an average diameter of $1\frac{1}{4}$ inch, and a weight not more than of 10 grams, and the factory we have referred to, produces on an average 50,000 pieces a day!

The mix used for the manufacture of Piston Cups should be made by skilled hands, each ingredient, composing the compound, accurately analysed and tested. The Cup should be moulded between polished chromium, stainless steel, or between polished aluminium ⁽¹⁾

(1) Always using the Mould Paste, for moulded goods, as described on page 141 Vol. I.

Each Piston Cup must be accurate to two-thousandths part of an inch,—(except for Golf Balls, this is the smallest tolerance allowed for a rubber article),—must fit a ring gauge for exact diameter, and pass a micrometer test for height. The Piston Cup must withstand up to 600 lbs. pressure per square inch. In a scientifically lighted room, skilful eyes should examine each Piston Cup through a microscope and reject every piece that has the tiniest defect, such as blisters, or a speck of dust. The good ones are then sent to a dark room for X-ray examination.

The following mix will be the right one for the manufacture of these delicate Piston Cups:-

Pale Crepe	10 ^k 000
Micronex	1 000
Kaolin	4 000
Zinc Oxide	0 500
Ozokerite	0 120
Sulphur	0 250
Flectol H	0 120
Ureka White	0 120
Stearic Acid	0 100

For the vulcanisation, we suggest 20 minutes at 150° C. or 302° F., but this should be determined by factory test, for the result may vary according to factory equipment.

Hot Water Bottles. These can be made from one of the following mixes:-

1. Smoked Sheets	10 ^k 000
Zinc Oxide	1 000
Whiting	8 000
Stearic Acid	0 100
Cycline Oil	0 200
Sulphur	0 250
Thiofide	0 060

Ultra Zinc DMC 0^k 010

RSL Colour 0 125

Cure 8 to 10 mins. at 298° F.

2. Pale Crepe 10^k 000

Zinc Oxide 0 500

Whiting 8 000

Stearic Acid 0 100

Paraffin Wax 0 050

Sulphur 0 150

Ureka White 0 150

Colour As desired.

Cure 6 to 8 mins. at 307° F.

3. Smoked Sheets 10^k 000

Zinc Oxide 0 500

Whiting 8 000

Stearic Acid 0 050

Cycline Oil 0 200

Paraffin Wax 0 075

Sulphur 0 250

Thiuram DS 0 025

RSL Colour 0 100

Cure 12 to 18 mins. at 258° F

or 6 to 10 „ at 287° F

or 4 to 7 „ at 307° F

4. Pale Crepe 10^k 000

Zinc Oxide 1 000

Whiting 8 000

Cycline Oil 0 200

Stearic Acid 0 050

Sulphur 0 200

RSL Colour 0 200

Ureka White 0 100

Cure 6 to 8 mins. at 307° F.

One of the aforesaid mixes, after being run out of the calender, in sheet form, at the required thickness and liberally coated with talcum powder, is cut into pieces in the shape of the desired pattern. Two such pieces are placed on each side of the core, previously coated with mould paste, moulded and vulcanised in the press, under hydraulic pressure. The core as well as the inner surfaces of the mould should be of mirror polished metal, either steel, tinned bronze, or aluminium. When vulcanisation is completed, the water bottle is removed from the mould and the core, still hot, is extracted from the cured rubber with the help of hot saponified water. The metal-threaded collar is then inserted in the rubber neck and the water bottle, after it has been washed and cleaned with glycerine, is ready for the market.

Typewriter Rollers. These are recovered with the following mix, which is calendered at the given thickness:-

Smoked Sheets	2½ 500
Carbon Black P33	2 250
Kaolin	3 000
Sulphur	0 175
Ureka White	0 050
Zinc Oxide	0 750
Rosin Oil	0 063
Rosin	0 063
Flectol H	0 038

The rubber is built on an aluminium mandrel having the same external diameter as the wooden roller of the typewriter to be recovered with rubber.

First, a ply of one-side-rubberised canvas, fixed around the mandrel, the unproofed side against the metal; then the rubber sheet placed upon the rubberised

ply, the whole securely wrapped in strong canvas, and vulcanised in open steam, raising slowly, for 15 minutes, to 306° F. and maintaining at that temperature for 25 to 30 minutes.

After cure, the rubber is removed from the mandrel, and it appears like a tube with an inner layer of cotton. The tube is polished on the lathe, care being taken that its outer surface is even, free from air-holes or blisters, and of the exact external diameter. When polished, the rubber tube recovers the wooden typewriter roller, on which it is kept in place with a small nail at either end.

Golf Balls. We have stated in the foregone pages that Golf Balls are allowed the smallest tolerance known in the rubber industry, as regards their accurate size and weight. It is not intended to describe the fabrication of these balls from *A* to *Z*, as only very few factories in this part of the world may be interested in it.

It may be stated, for the sake of information, that for producing a golf ball, sometimes a month, or even more, is needed, and that before completion, it needs several handling operations, as many laboratory tests, and more than a dozen control tests. And these golf balls, which cost us only a few annas, we may lose in a split second!

The first part to be manufactured is the sac. This is produced on an aluminium former dipped in latex, immersion time being reckoned by means of a stop watch, in order to determine its exact thickness. Then, as in the case of other dipped goods, it is plunged into acetic acid to coagulate the latex, and vulcanised. After curing, the sac is stripped off the former, and the right amount of paste is introduced

into it by means of a filling machine. (It is said that one of the American manufacturers, specialised in the fabrication of golf balls, fills the sacs with pure honey!) At this stage the sac so filled is again put into the mould to be frozen at a temperature of not less than 150° C. below zero, after which it comes out moulded and is ready to be wrapped, by a special winding machine, with the rubber thread, prepared from a calendered sheet which had been previously vulcanised on the drum.

The sac, covered with the thread at the required diameter, is embedded between two half shells made of a compound consisting of hevea rubber with gutta percha and the addition of fillers, sulphur and the accelerator. These hemispherical shells were pre-heated in special moulds under high pressure and low temperature. When the ball is finally put in these two hemispherical shells, it is again vulcanised in the mould and is then ready for brushing, testing, painting and boxing. The size is then gauged to a hair's breadth! In America, the standard golf ball should not be less than 1.68 inches in diameter and more than 1.62 oz. in weight.

It is doubtful whether, in view of this complicated fabrication, many rubber manufacturers will be inclined to start such a kind of production? After all, how many of the 100 and odd rubber factories installed in India, are able to perform a single laboratory test, for the reason that they do not possess a laboratory? Without a laboratory, most of them are working like blind men, as it is then impossible to check the chemicals which are being used and which are the main items

in the factory, because they help the accelerators to do the work they are intended for.*

Mottled Running Corridors with coloured Borders.

The fabrication of marbled carpets and corridors is explained in Vol. I, page 236. If a coloured stripe is to appear on either side of the running corridor, this can be produced on the calender, at the same time the marbled sheet is calendered. For such fabrication the calender should be provided with four guides, *A*, *B*, *C*, and *D*, from left to right, instead of the usual two, *A* and *D*, the four guides facing the space between the two upper rollers of the calender. These guides are to be arranged in such a way that the distance between the guides *A* and *D* is governed by the width of the bordered running corridor to be produced. The two inner guides *B* and *C* are separated from *A* and *D* to produce just the coloured stripes of the given width, both the surfaces of *B* and *C* being made to slope down, so that the part which is nearer to the calender rollers is as thin as possible.

The calender is fed with the marbled mix, by introducing it between the guides *B* and *C*, whereas the coloured mix is introduced at the same time, between the guides *A* & *B* and *C* & *D*, so as to produce the coloured stripes.

* To those who realise the necessity of having a laboratory, we would suggest that for their analysis they follow the British Standard Methods of Testing Vulcanised Rubber as well as Latex, Raw Rubber and Unvulcanised Compounded Rubber. Other literature and information can be obtained from the Institution of Engineers (India), 8 Gokhale Road, P. O. Box No. 669, Calcutta.

This method has the advantage of increasing the production, as no stripes are to be joined, by hand, to the marbled sheet after it has been calendered, and no effort is required to make the stripes firmly adhere to the main sheet. The mix recommended for such fabrication is M2, (see page 236) which can be coloured, if required, by the addition of dyestuffs.

“Proofed Fabrics for Gun Powder Bags.” The need for gunpowder bags is not the direct outcome of the War, but even in peace time gun powder is produced, and consequently has to be packed. The best packing for this purpose is the rubberised bag.

The solution used for proofing the fabric, from which the bags are made, should be free from grit and particles of mineral matter, and must be smoothly and evenly applied, say at the rate of 10 oz. per sq. yd. The proofing must penetrate the fabric, adhere firmly to it, should be well vulcanised—preferably at room temperature, as in that case the textile matter is not deteriorated by the action of steam during the cure in the vulcaniser—and, when detached from the fabric, should be elastic. The proofed fabric must not be acidic to methyl-orange and should not contain more than 0.2%, calculated as sulphuric acid, of water-soluble acids affecting phenolphthalein, nor should it be alkaline to phenolphthalein and must not contain more than 0.2%, calculated as anhydrous sodium carbonate, of water-soluble alkaline substance affecting methyl-orange.

The solution should contain not less than 45% of pure rubber and not more than 52% of mineral fillers.

The amount of sulphur extractable by acetone must not exceed 0.75%, and "*the coefficient of vulcanisation**" must not be less than 2 or greater than 3.5.

* The "*Coefficient of Vulcanisation*" is the combined sulphur in a vulcanised rubber compound, and is defined as the units of weight of sulphur combined with 100 units of weight of rubber hydrocarbon.

$$x = 100 \frac{a}{b}$$

Where x is the coefficient of vulcanisation,
 a is the combined sulphur per cent, and
 b is the per cent of rubber hydrocarbon.

Soft rubber compounds have coefficients varying up to 4 and ebonite compounds have coefficients varying between 25 and 47.

When it is thus stated that the coefficient of vulcanisation should not be less than 2 or not greater than 3.5, this means that the combined sulphur should lie between these limits. A specification of this kind, therefore, requires the addition of a certain minimum of sulphur during compounding, in order to determine, to some extent, the degree of vulcanisation that is to be effected. There are three kinds of sulphur in a vulcanised rubber compound:

1. *The total Sulphur*, which is the amount of sulphur added during compounding, plus any sulphur-content in accelerators or other compounding ingredients added to the mix,

2. *the combined Sulphur*, which is the amount of sulphur which has actually combined with the rubber hydrocarbon during the process of vulcanisation;

3. *the free Sulphur*, which represents the balance of sulphur, being the difference between the total sulphur of the compound and the combined sulphur, which remains in the compound, after vulcanisation, in an uncombined state.

Free Sulphur in vulcanised rubber is determined by the estimation of sulphur is acetone extract by either the Bromine or the Nitric Acid method; whereas combined sulphur is estimated indirectly by determination of the total sulphur on a sample of vulcanised rubber which has been subjected to extraction with acetone, chloroform and alcoholic potash, and then applying a correction for the sulphur present in the total fillers.

The solution should contain only rubber of the first grade, with no reclaim. When the proofing is extracted with hot acetone for 10 hours, it must not yield more than 5% of organic matter (exclusive of mineral waxes) calculated on the rubber present.

When the proofing, which has been extracted by acetone, as mentioned above, is treated for four hours with boiling alcohol semi-normal potassium hydroxide solution, the organic matter obtained on acidification of the liquid should not exceed 1.5% calculated on the rubber present. As already stated the mineral matter should be free from grit, being pure zinc oxide with small addition of other ingredients required to stimulate the accelerators used for vulcanisation. The rubberised fabric should resist the following test:-

Two pieces of canvas, 6 inches wide, are each coated twice with the above solution for a length of 4 inches from one end. The rubberised surfaces are well pressed together, the unrubberised areas being at opposite ends, and left for 24 hours under a weight of 56 lbs. Thereafter they are securely suspended by one of the uncoated ends, and a weight of 56 lbs. is attached to the other end. The joint should support the weight for at least 24 hours.

Transparent Stocks. There has been considerable demand for the production of small rubber novelties, rubber teats and so forth, of transparent or semi-transparent rubber. These articles must be vulcanised at a relatively low temperature, otherwise instead of a translucent light-amber product one obtains a much darker amber material. Therefore, ultra-accelerators are necessary.

For transparent rubber it is impossible to use any amount of compound. However, a certain quantity

of soluble zinc oxide is essential to practically all rapid accelerators. The zinc oxide may be added in the form of rubber soluble zinc such as zinc stearate, or may be added in the form of very finely divided, almost colloidal zinc oxide. It is found that this extremely fine zinc oxide initially has very little covering power, and furthermore, during the vulcanisation, it apparently is dissolved by the rosins present in the rubber, so that it is completely in solution when vulcanisation is completed. It is generally found that about 2% of zinc oxide, or its equivalent in soluble zinc soaps, is necessary to get full activation of the accelerator. However, almost full activation can be obtained with about 1% of zinc oxide and fairly good activation with from $\frac{1}{2}$ to 1%. Below $\frac{1}{2}$ %, the activation is insufficient to be of much value.

The accelerator that gives one of the nicest of the transparent rubbers is R-2. This is perhaps because it is an oil in itself and dissolves thoroughly in the rubber, causing no overcure where particles of a crystalline accelerator would be present. The use of R-2 in work of this character is illustrated by the formula appearing on page 235, the cure of which is usually 30 minutes at 239° F or 12 minutes at 258° F. This cure varies slightly, depending upon the amount and fineness of the zinc present. It is, moreover, affected slightly by the absence, or presence, of lead and cadmium content in the zinc oxide used. All commercial varieties of zinc oxide vary considerably in their fineness and content of lead and cadmium and change should not be made from one grade of zinc oxide to another in a carefully adjusted formula, without checking the possible effect on the vulcanisation. The sulphur content is very low, being only 1 to 100 of rubber. This is sufficient in all ordinary cases, but

may be increased slightly if desired. The stock obtained by the said formula is absolutely non-blooming and of a light amber colour.

The Fabrication of Observatory Balloons has to be done very carefully, because of the purpose for which they are intended, namely: to record weather forecast. They are generally filled with helium.

Under the observatory balloon is attached a parachute to which is suspended a little radio transmitter for registering continuous records of altitude, pressure, temperature and humidity. Under the radio transmitter is suspended another small balloon, made of inferior quality of rubber, hermetically sealed and filled half with helium, and half with sand.

When that heterogeneous assemblage is released, it ascends into the atmosphere. After reaching a certain altitude, the small balloon, containing sand bursts, releasing the helium-filled balloon of its sand ballast. This balloon, which before its departure was inflated to the extent of a diameter of one meter, now climbs to an altitude, where it attains a diameter five times as great, and where, due to the low pressure existing at such high altitudes, it also bursts. The burst liberates the parachute and the radio transmitter attached to it. These fall to the earth and are expected to be returned, by the finder, to the Observatory from where the balloon, with the radio transmitter, was released into the atmosphere.

Observatory Balloons must be strong and should be made of first class rubber mixes capable of expanding, at least, five times their original size.

We suggest the following mix for such balloons:

Pale Crepe	...	10 ^k 000
Colloidal zinc oxide	0 ^k 050 to 100 grams
Sulphur	0 ^k 100
R-2	0 ^k 075

The mix is dissolved in a suitable solvent and, like the "Gofferdam Plates" is spread on a proofed fabric, from where it is stripped. The proofing of the fabric used for this purpose should be done correctly, otherwise the sheets produced on it will be rough. After the fabric has been rubberised, it should be cured and then varnished with shellac which will facilitate the stripping of the rubber sheet to be produced on it.

When the "Gofferdam sheet" is peeled off the proofed and varnished fabric, it must be heated upon curing plates to remove the calendering effect. If this is overlooked, the balloon may be badly distorted, or deformed, during its vulcanisation which is suitably done in French Chalk. The time of cure of the above mix is, as already stated, about 30 minutes at 239° F. or 12 minutes at 258° F, but this should be determined in the factory.

Sometimes, Observatory Balloons of small sizes, are made by the dipping process, either with the rubber mix, as stated above dissolved in a solvent, or in latex compound.

The manufacture of these balloons requires skilled hands.

The fabrication of "Special Packing" used for multitubular boilers of the "Mathot" and the "Babcock" types is very interesting. The size of the packing is usually 100 mm. inner diameter, 120 mm. outer

diameter, and thickness 2 mm. with a single insertion ply. It is important that the mix for making this special packing should contain an accelerator having a retarding effect, of the Ureka type, and we would suggest the following formula:—

M2.	Smoked Sheets	10 ^k 000
	Zinc Oxide	5 000
	Whiting	5 000
	Paraffin Wax	0 200
	Cycline Oil	0 400
	Stearic Acid	0 200
	Barium Sulphate	22 500
	Sulphur	0 300
	Ureka	0 150
	Flectol H.	0 150

Cure: 30 to 45 minutes at 293° F.

The mix is calendered in sheets 1 mm. thick. This sheet is joined on the mandrel of 110 mm. diameter, over which is placed a ply of open woven rubberised fabric, proofed with the following solution:—

	Smoked Sheets	12 ^k 500
	Carbon Black	6 250
	Zinc Oxide	3 000
	Barium Sulphate	22 000
	Stearic Acid	0 250
	Sulphur	0 300
	Ureka	0 037½
	Paraffin Wax	0 250

Another sheet of rubber, 1 mm. thick of the same M₂ mix, as stated above, recovers the rubberised insertion fabric, and the whole is wrapped in canvas, dipped previously in the mould paste (see Vol. I, Chapter VIII,

page 141). The mandrel so wrapped is immersed, for 20 minutes, in boiling water. The object of this immersion is to remove any traces of the join produced by the overlapping of the outer and inner rubber sheets. The temperature of the boiling water, (212° F), combined with strong canvas wrapping, is sufficient to effect this, the boiling bath not affecting the rubber mix in the least, which still remains unvulcanised during the immersion. When removed from the boiling water bath, the drum, cooled down, is unwrapped and the rubber cylinder, with its inserted rubberised ply, well dusted with talcum powder, is forced upon a wooden mandrel of 110 mm. outer diameter, to be cut on the lathe in rings of 10 mm. width. The rings so cut are removed from the mandrel, again powdered with talcum, and then put on an aluminium mandrel of 100 mm. diameter, standing perpendicularly. Each ring is then flattened, so that its lower edge, when in contact with the aluminium mandrel, becomes the inner circumference of the packing ring, which has thus an inner diameter of 100 mm., whereas the upper edge of the ring becomes the outer diameter of the packing ring, of 120 mm. diameter. The mandrel thus filled with the flattened rings, well pressed on top of each other, is vulcanised in open steam for 45 minutes at 293° F. After cure, the rings are removed from the mandrel and assembled by gross. They are then ready for the market.

This kind of fabrication eliminates all the waste incurred by other processes.

Rubber Hoses—Oil & Petrol Resisting can be manufactured with an inner layer of Synthetic Rubber, as follows:—

A. With Thiokol.

The following compound is suggested:—

Thiokol	100 ^k 000
Rubber	} as a master batch	5 000
D.P.G.		0 250
Thiuram		0 100
Zinc Oxide	10 000
Carbon Black	25 000
Stearic Acid	0 500
		140 ^k 850

The inner layer, of not more than 2 mm. thick, is extruded from the Forcing Machine, directly in a cold water bath, which will eliminate practically all odour, or gas, emanating from the Thiokol compound. The extruded tube should be dried partially, so that there remains from 0.3 to 0.5% of moisture on its surface, which is essential to bring about the cure of the Thiokol mix. The tube is then forced upon a well polished brass or copper mandrel*, coated with mould paste, which is then covered with one or two plies of cotton fabric, rubberised with the following mix dissolved at the rate of 4 kilos of dry compound per gallon of solvent.

Smoked Sheets	10 ^k 000
Zinc Oxide	0 500
Ureka	0 120
Sulphur	0 250
Flectol H.	0 120
Stearic Acid	0 100
	11 ^k 090

*In the case of rubber hoses made of an inner layer of Thiokol, brass or copper mandrels should be used, as the Thiokol layer in contact with brass or copper produces, under the influx of heat, a sulphide formation, which facilitates the removal of the vulcanised hose from its mandrel.

It is of advantage that the solution compound should neither be heavily loaded nor cure too quickly. This will facilitate a strong adhesion of the rubberised fabric to the Thiokol compound.

Over the ply, or plies, of rubberised fabric are braided from one to three layers of cotton, well impregnated with the above solution, on top of which is placed the upper layer of 1 mm. thick of the following rubber compound:—

Smoked Sheets	10 ^k 000
Kaolin	4 000
Zinc Oxide	0 500
Paraffin Wax	0 120
Ureka	0 120
Sulphur	0 250
Flectol H	0 120
Stearic Acid	0 100
Colour	To suit

The rubber hose thus manufactured is now *strongly wrapped* in resistant cotton fabric* prepared as stated on page 141, Chapter VIII, Vol. I, and kept overnight, which will greatly facilitate the bonding of the synthetic compound to the other parts of the rubber hose. The vulcanisation is done on the following day for 50 to 60 minutes at 287° F., or eventually at 298° F.

After cure, the hose must be allowed to cool down completely before unwrapping, as otherwise the inner layer of Thiokol will become porous.

After removing from the mandrel, the rubber hose is cleaned and is then ready for despatch.

*In order to obtain a still firmer adhesion of the cotton plies to the inner layer of Thiokol, the cotton wrapping should be done in spiral form by using the Triple Tandem Rubber Hose Machine (see fig. XXI, page 176, Vol. 1).

B. With Neoprene.

The following mix is recommended:-

Neoprene Type E	100k 000
Brown Factice	20 000
Light calcinated magnesia		10 000
Thermatomic Black	70 000
Wood Rosin	5 000
Mineral Oil	5 000
Neozone D	2 000
Nonox NSN	2 000
Sulphur	1 000
Paraffin Wax	0 500
Zinc Oxide	10 000
		<hr/> 225 500

The above mix is extruded from the Forcing Machine as explained in Chapter IX—Neoprene. The other processes of manufacture of hoses with Thiokol apply in this case also, except that the vulcanisation in this instance is 60 minutes at 280° F.

Fabrication of Rubber Hoses

vulcanised in boiling water.

For this fabrication, split batch mixes are necessary. The inner layer will be composed of:—

A.

Smoked Sheets	5k 000
Kaolin	4 000
Red IE	0 300
Paraffin Wax	0 120
Sulphur	0 250
Flectol H	0 120

B.

Smoked Sheets	5k 000
Zinc Oxide	0 500
Stearic Acid	0 100
Vulcafor ZIX	0 100

These two mixes can safely be stored separately, but if mixed, the cure starts immediately. When mixed, the resulting compound is calendered at the given thickness for the inner layer of the rubber hose to be manufactured, which is made as explained in Chapter IV, Volume I, pages 175 - 179, with the exception that the cotton plies should be rubberised with the combined mixes A and B mentioned above. The upper rubber layer (black) should be made of a combination of both the mixes C and D shown below:—

C.

Smoked Sheets	5 ^k 000
Carbon Black	1 000
Kaolin	4 000
Paraffin Wax	0 120
Sulphur	0 250
Flectol H	0 120

D.

Smoked Sheets	5 ^k 000
Zinc Oxide	0 500
Stearic Acid	0 100
Vulcafor ZIX	0 060

and calendered at the required thickness. The rubber hose thus prepared is wrapped, as already stated, in canvas prepared as detailed on page 141, Chapter VIII, Vol. I, and immersed in boiling water for one hour. After cure, the hose is unwrapped, taken off the mandrel, cleaned, and is ready for the market.

To obtain a complete cure, the inner rubber layer must have a higher accelerator-content. Because of its proximity to the aluminium mandrel, it is not likely to get as quickly heated, when immersed in boiling water, as the outer layer, wrapped only in canvas. Without this precaution, the inner layer, by not being fully vulcanised, will tend to become spongy.

The vulcanisation of rubber hoses, in boiling water, has many advantages:

1. The necessity for a costly hose vulcaniser made of steel, of say 100ft. long, can be obviated. This type of vulcaniser is usually provided with railways,—also 100ft. long,—and a charriot which conveys the hoses in and out of the vulcaniser. The rails occupy an area of the factory which cannot be used for other purposes.

2. The capacity of the boiler, for producing steam for the Presses and the Vulcanisers, can be reduced, for much less steam is necessary to boil water in a tank, than to fill a hose vulcaniser, say of 100ft. length and 2 ft. diameter, at 40 to 60 lbs. pressure.

3. Rubber hoses with cotton ply insertions, vulcanised in boiling water, are more resistant than such hoses vulcanised in steam, for vulcanisation in a hose vulcaniser is effected at an average temperature of 140°C , whilst the vulcanisation in boiling water is done at 100°C ,—just the temperature needed to keep the water boiling—and as raw cotton, whether bleached or unbleached, deteriorates under the action of heat, from 110°C and upwards, the strength of a rubber hose, vulcanised at higher temperature will be adversely affected.

4. No thermometers are needed to check the temperature as in the case of steam vulcanisers made of steel. The only precaution to take, when vulcanising in boiling water, is to see that the water boils throughout the period of vulcanisation.

Tanks for vulcanising rubber hoses, in boiling water, should be made of teak wood, and should be lined inside with zinc sheets.

At the bottom of the tank, and running throughout its whole length, there should be a steam pipe with many holes to allow the steam to escape. This pipe should be connected to the main pipe coming from the boiler, and a uniform supply of steam throughout the length of the steam pipe is thereby assured. To facilitate the quick boiling of the water, it is advisable to cover the tank. This vulcanisation tank should also be connected to the water tank, so that, after each vulcanisation, the hot water can be removed and replaced by cold water, in which the subsequent cure has to be started.

Soda Water Bottles Rings are made of the following mixes:—

Pale Crepe	10 ^k 000
Zinc Oxide	0 500
Calcium Carbonate	5 100
Stearic Acid	0 100
Cycline Oil	0 300
Sulphur	0 300
Flectol H	0 200
Barium Sulphate	5 000
Vulcafor DPG	0 100
Vulcafor ZDC	0 020
Orange 8B	0 200
Red IE	0 100

Cure in French Chalk in open steam for 35 minutes at 292 °F.

White Soda Water Bottle Rings.

Pale Crepe	10 ^k 000
Zinc Oxide	4 000
Sulphur	0 200

Stearic Acid	0 ^k 100
Cycline Oil	0 400
Flectol H.	0 200
Ureka White	0 075

Cure in French Chalk in open ste for 20 minutes at 287 °F.

Red Soda Water Bottle Rings.

Pale Crepe	10 ^k 000
Zinc Oxide	0 500
Calcium Carbonate	5 000
Stearic Acid	0 100
Cycline Oil	0 300
Sulphur	0 250
A 32	0 025
Flectol H	0 200
Orange 8B	0 100

Cure in French Chalk in open steam for 45 minutes at 286 °F.

Soda Water bottle rings are extruded from the Forcing Machine. The tube so produced is placed on an aluminium mandrel to be vulcanised in talc, according to the mix, without being wrapped in canvas. After vulcanisation the tube is cut into rings of given thickness, either on the Cutting Machine or on the lathe. If red rings are to be coated *white* outside, the tube, after vulcanisation and before being cut into rings, is dipped in a solution made of 50% pale crepe and 50% zinc oxide, dissolved in solvent.

Ebonite Mix for Insulators.

Formula		% on the rubber	% on the weight of the mix
Pale Crepe	10 ^k 000	—	49½ %
Sulphur	4 000	40	19.8%
Accelerator A7	0 200	2	0.99%
Kaolin	6 000	60	29.7%

Cure in moulds: 4 hours at 298° F.

Ebonite without accelerators or fillers.

Pale Crepe 10^k 000

Sulphur 4 000

Cure: 13 hours at 280° F. according to the thickness of the sheet or the rod.

A test piece of the above mix, 15 mm. square and 200 mm. long, would not bend by more than 5 mm. under a load of 450 grams maintained at a temperature of 55° C. for 6 hours.

By the addition to the above mix, of organic accelerators, such as diphenyl-guanidine or butyraldehyde aniline, the vulcanising time can be shortened by about 4 hours, and when ordinary fillers are used in the said mix, the ebonite obtained can be made to pass the test at much higher temperature, say up to 80 to 90° C.

Battery Cases. Three distinct moulds are required to produce a complete *Battery Case*. These are: the mould for the main part, the mould for the lid and the mould for the plugs. As already suggested in Chapter VII, these moulds should be made of an aluminium alloy, well polished.

The following mix is used to produce the ordinary type of Battery Cases:-

Smoked Sheets	10 ^k 000
Sulphur	4 000
A 7	0 200
Kaolin	6 000

The compound is calendered in sheets of about 5 mm. thick and the main part is prepared by hand from these sheets on a wooden form, the edges stuck together with benzine, and then moulded. The mould for the lid is generally filled directly with the calendered sheet drawn at the required thickness, whereas a piece of ebonite compound fills the mould for the plug. The moulds are then vulcanised, either in the press or in the vulcaniser, in open steam. Cure: 4 hours at 298° F.

Battery cases can also be made from a 95% *reclaim compound* of the following composition:-

Rubber	0 ^k 500
Reclaim	9 500
Sulphur	000
A 7	200
Kaolin	000

The manufacture of this type of battery cases is the same as described above, except that they are made from sheeted ebonite-reclaim of required thickness, the edges of which are coated with a solution of ebonite to help the different parts sticking together before they are moulded. The solution should be made of the following mix dissolved in solvent, at the rate of 3 kilos compound per one gallon of solvent.

Smoked Sheets	10 ^k 000
Sulphur	4 000
A 7	0 200
Kaolin	6 000

For preparing the lid and the plugs, the ebonite sheets are pasted together, with the above solution, until the required thickness is attained. The three moulds, when filled, are vulcanised for 1 hour 30 minutes, (or less as the case may be) at 293° F. in open steam, or in the press.

Ebonite Rods and Tubes are made from the following mix, which can be extruded from the Forcing Machine:-

Pale Crepe	10 ^k 000
Sulphur	4 000
A 7	0 200
Ebonite Dust	6 000
Vulcatac CH	0 300

They are vulcanised, either wrapped in canvas prepared as detailed on page 141 Vol. I, or without wrapping, in open steam, in talc. Cure: from $3\frac{1}{2}$ to 4 hours at 293° F, according to size.

Mix for Raleigh Cycle Brakes.

Red.

Smoked Sheets	5 ^k 000
Zinc Oxide	0 500
Calcium Carbonate	...	1 000
Sulphur	...	0 250
Vulcafor MBTS	0 075
Kaolin	4 000
Magnesium Carbonate		2 000
Vulcatac III	0 150
Orange 8B	0 300
Red IE	0 075

Cure: 1 hour at 293° F.

Black.

Smoked Sheets	10 ^k 000
Sulphur	0 700
Vulcatac III	0 300
Mineral Rubber	0 200
Zinc Oxide	17 000
Litharge	1 400

Cure: 25 minutes at 292° F.

The brakes, on account of their special shape, can be moulded, but can also be extruded from the Forcing Machine, in which case they are vulcanised in talc, in open steam.

Mix for Adhesive Tape.

Smoked Sheets	15 ^k 000
Tar	2 000
Grease	1 500
Rosin	2 000
Barium Sulphate	40 000
Flectol H	2 000
Carbon Black	5 000

The mix is dissolved at the rate of 4 Kilos of compound per gallon solvent, and applied on thin cotton fabric, either on one, or both sides, after which it is rolled on cardboard tubes and cut into discs on the lathe at the required thickness. Each disc is then packed in tin, or aluminium foils, ready for the market.

Mix for Insertion Sheetting.

Smoked sheets	12 ^k 500
Reclaim	12 500
Carbon Black	6 250

Zinc Oxide	15 ^k 000
Barium Sulphate	10 000
Flectol H	0 250
Stearic Acid	0 250
Sulphur	0 300
Ureka	0 037½
Paraffin Wax	...	0 375
Belting Waste	10 000

Cure: 45 minutes at 293° F.

**Solution for rubberising the insertion canvas
for the above sheeting.**

Smoked sheets		12 ^k 500
Carbon black		6 250
Zinc Oxide		0 300
Barium sulphate		22 000
Stearic acid		0 250
Sulphur		0 300
Ureka		0 037½
Paraffin Wax		0 250

This mix is dissolved at the rate of 3 kilos to one gallon solvent.

**Black mix for Rubber Sheet without insertion
(used by the R. A. F.)**

Smoked sheets	5 ^k 000
Reclaim	0 550
Flectol H	0 075
Zinc Oxide	0 250
Paraffin wax	0 100
Cycline oil	0 200
Stearic acid	0 100
Sulphur	0 150

Ureka white	0 ^k 075
Barium sulphate	6 000
Carbon black	2 500

Cure: 35 minutes at 298° F.

Tyre Stocks with A-16 Accelerator.

A-16 is a very satisfactory tyre accelerator for normal service conditions, particularly where the higher vulcanising temperatures are being used. By this we mean the more or less normal vulcanisation temperatures of 285 to 295° F. We feel that A-16 will give excellent service in all ordinary tyre stocks, and suggest its use in such cases, except for the very largest bus and lorry tyres where the use of Ureka HR will give somewhat superior results.

Typical formulas for tyres are as follows:—

	Friction	Skim Coat	Cushion	Tie Strip	Tread
Smoked Sheets	50	75	100	100	100
Softer Rubber	50	25	—	—	—
Zinc Oxide	8	12	20	45	8
Stearic Acid	0.5	1.5	1	1	2
Tackol	—	2	2	1	2
Pine Tar	3	—	—	—	—
Sulphur	4	3.75	3.5	3.75	3.5
Carbon Black	—	—	—	—	50
A-16	0.75	0.75	0.75	0.70	1.25
A-5-10	—	—	—	—	0.50
	116.25	120.00	127.25	151.45	163.75

The proper cures for tyres made from these stocks will be approximately as follows:—

Light-weight 4-ply—15 min. rise, 1 hour at 290° F.

Heavy 4-ply and light-weight 6-ply—15 min. rise, 1 hr. 15 mins. at 290°F.

Heavy-weight 6-ply and ordinary 8-ply tyres—15 min. rise, 1 hr. 35 mins. at 290° F.

Heavy-weight 8-ply tyres—15 min. rise, 1 hr. 50 mins. at 290° F, 30 min. soak.

10-ply 6 in. truck tyres—1 hr. rise, 2 hrs. cure at 287° F.

12-ply 7 in.—1 hr. 20 min. rise, 2 hrs. cure at 287° F, 30 min. soak*.

Bead Stocks.

		Clincher Bead	Wire Bead
Broken down Smoked			
Sheets	20	12
Whole Tyre Reclaim		40	40
Mineral Rubber	10	—
Zinc Oxide	5	5
Soft black	20	12
Stearic Acid	—	1
Tackol	2	2
Lime	5	2
Sulphur	10	18
A-16	0.625	0.375
A-5-10	1	1
		113.625	93.375
Set Cures: }		5 mins. at 316° F.	10 mins. at 316° F.

* By soak is meant that the steam is cut off in the retort, but the tyres are allowed to remain in the mould for a period of thirty minutes. This causes the outside to cool somewhat and no further cure will take place. However, the heat is retained on the inside and this will enable the inside of the tyre to come up to its proper cure without any further cure taking place on the outside.

A-16 in Inner Tube Stocks.

A-16 is an especially desirable accelerator in inner tube stocks. Rapid cures can be obtained, and at the same time the stocks may be handled without difficulty. The following are two moulded tube formulas as well as two formulas for cure in open steam on mandrels. The moulded tube formulas contain a certain quantity of blanc fixe, which reduces the pound price of the mixture, and permits easy extrusion of the stock. The mandrel-cured stocks shown, do not contain mineral matter, but they can be compounded to the same extent as the moulded tube formulas without other alteration in the ingredients. This addition of from 20/40 parts of barium sulphate or a somewhat lesser quantity of whiting or zinc oxide will materially assist the working properties of the stock.

Moulded Tube Formula with A-16

	Grey Blooming	Red Non-Blooming
Smoked Sheets	100 ^k	100 ^k
Zinc Oxide	5	5
Blanc Fixe	40	40
Red Iron Oxide	--	3
Stearic Acid	0 75	0 75
Sulphur	3 5	2 25
A-16	1 10	1 5
Cures in mould: }	5 minutes at 307 ° F.	7 minutes at 307 ° F.

Open Steam Mandrel-Cured Inner Tubes with A-16.

	Grey Blooming	Red Non-Blooming
Smoked Sheets	100 ^k	100 ^k
Zinc Oxide	5	5
Sulphur	3 5	2 5

		Grey Blooming	Red Non-Blooming
Tackol	1 ^k	1 ^k
A-16	0 625	0 75
Red Iron Oxide		—	2
Cures:	{	25 min. at 274° F.	30 min. at 287° F.

The foregoing formulas and curing specifications are designed to suit average factory conditions, but due to the variations which always exist in different factories, products should be carefully checked before running a large production. It should be understood that the time required for curing different sizes of tyres will necessarily vary somewhat and the figures given are general average.

It must be further noted that the milling procedure will vary in different plants, and this will of course necessitate some slight variation either in the formula or in the time of the cure.

Miscellaneous Formulas Using A-16

Black Heel

Smoked Sheets	16 ^k
Whole Tyre Reclaim		50
Mineral Rubber	3
Carbon Black	9
Zinc Oxide	5
Clay	16
Stearic Acid	1
Suphur	1 5
A-16	0 56

Cure: 10 to 12 mins. at 316° F.

The above formula may be cheapened still more by using 30 parts whiting instead of the clay and carbon black.

Tan Sole

Smoked Sheets	...	25 ^k
Mineral Rubber	6 5
Magnesium Carbonate		25
Clay	10
Blanc Fixe	8
Red Oxide	4
Zinc Oxide	16
Paraffin Wax	0 5
Stearic Acid	1
Sulphur	1 25
A-16	0 5
Flectol H	0 4

Cure: 15 to 18 minutes at 307 ° F.

Good Quality Black Sole

Smoked Sheets	100 ^k
Mineral Rubber	10
Carbon Black	105
Zinc Oxide	10
Stearic Acid	1
Tackol	3
Flectol-B	1
Sulphur	3 5
A-16	2

Cure: 20 minutes at 307 ° F.

**Heavily Compounded Stocks Suitable for
Flooring, Tiling, Etc. with Thiofide.**

Rubber	100 ^k
Zinc Oxide	10 - 50
Whiting	150
Clay	150
Lithopone	0 - 100

Stearic Acid	2 ^k
Cycline Oil	4
Sulphur	3
Thiofide	1 75
Colour	To suit

Cure: 12 to 18 minutes at 307 ° F.

The larger quantities of zinc oxide and lithopone are for white stocks. No other change need be made in the formula.

Extruded Hose—Suitable for Water Hose, Etc. with Thiofide

Rubber	100 ^k
Whole Tyre Reclaim		50
Zinc Oxide	5
Clay	100
Whiting	100
Tackol	4
Mineral Rubber	10
Stearic acid	1
Flectol H or B	1
Sulphur	6
Thiofide	0 3

Cure: 20 to 60 minutes at 287 ° F.

Cheap Black Heel with Thiofide.

Rubber	100 ^k
Whole Tyre Reclaim		350
Zinc Oxide	10
Clay	175
Carbon Black	35
Stearic Acid	3
Flectol H	2

Sulphur	8 ^k 5
Thiofide	1 75

Cure: 10 to 12 minutes at 307 ° F.

Quality White Flexible Flooring with

Pale Crepe	...	100 ^k
Zinc Oxide	50
Lithopone	...	200
Whiting	180
Stearic Acid	...	2
Cycline Oil	4
Paraffin Wax	2
Sulphur	3
Thiofide	1 50

Cure: 15 minutes at 307 ° F.

Elastic Band Stock with Thiofide.

Pale Crepe	100 ^k
Zinc Oxide	2 5
Stearic Acid	0 5
Sulphur	2 5
Thiofide	0 5
Flectol H	0 25

Cure: 20 minutes at 298 ° F.

Insulated Wire Stocks with Thiofide.

Rubber	100 ^k
Zinc Oxide	100
Whiting	...	100
Stearic Acid	0
Paraffin Wax	3
Sulphur	...	3

Thiofide	0 ^k 9
Flectol H	1

Cure: 30 to 90 minutes at 330° F.

Wire Carbon Black Stock cured without the addition of Sulphur.

Smoked Sheets	100 ^k
Zinc Oxide	8
Carbon Black	45
Stearic Acid	3
Tackol	5
Flectol B or H	2
Thiuram DS	4
Thiofide	1

Cure: 15 minutes at 274° F.

Non-tarnishing Wire covering stock without the addition of Sulphur.

Pale Crepe	100 ^k
Zinc Oxide	50
Talc	50
Whiting	100
Stearic Acid	1
Paraffin Wax	2 5
Flectol B or H	1 5
Thiuram DS	2

Cure: 30 to 45 minutes at 266° F.

Transparent Stock without Sulphur.

Smoked Sheets	100 ^k
Colloidal Zinc Oxide		1
Stearic Acid	0 5

Thiuram DS	3 ^k
Thiotax	0 5

Cure: 30 minutes at 266° F.

Thiuram DS Stocks in open Steam and mould cures

Rubber	100 ^k
Zinc Oxide	5
Whiting	80
Stearic Acid	...	0 5
Cycline Oil	2
Paraffin Wax	0 75
Sulphur	2 5
Thiuram DS	...	0 25
R.S.L. Colour	1

Cure: 12 to 18 minutes at 258° F.

or 6 to 10 „ „ 287° F.

or 4 to 7 „ „ 307° F.

Translucent Stocks.

Pale Crepe	100 ^k
Colloidal Zinc Oxide		0 75
Sulphur	2
Thiuram DS	0 25

Cure: 45 minutes at 258° F.

or 20 274° F.

Hot Air Work.

Here it is desirable to increase the amount of Thiuram DS slightly, i.e. from about 0.3 to 0.6% which will give very satisfactory results.

White Sheetting.

Pale Crepe	100 ^k
Zinc Oxide	10
Whiting	100
Titanium Pigment		35
Stearic Acid	0 5
Sulphur	1 25
Thiuram DS	0 60

Cure: Slow rise, then 30 minutes at 250° F.

Black Soles.

Rubber	100 ^k
Zinc Oxide	35
Whiting	120
Carbon Black	15
Stearic Acid	1
Cycline Oil	3
Sulphur	2 25
Thiuram DS	0 7
Flectol B or H	1

Black Uppers.

Rubber	100 ^k
Zinc Oxide	25
Whiting	60
Carbon Black	2
Clay	15
Stearic Acid	...	1
Cycline Oil	3
Sulphur	...	2
Thiuram DS	0 6
Flectol B or H	1

Both the above stocks may be cured in hot air using a 30 minutes rise and 30 to 60 minutes at 250° F. with 30 lbs. air pressure.

Thiuram DS used with another Accelerator.

Using Thiuram DS in this fashion, the combination is equally suitable for press, open steam and hot air cures, as may be seen from the following formulas:-

Hollow Balls, Bulbs, etc.

White.

Pale Crepe	100 ^k
Zinc Oxide	40
Lithopone	...	40
Whiting	100
Stearic Acid	1
Cycline Oil	4
Sulphur	3
Thiofide	1 6
Thiuram DS	0 2

Coloured.

Pala Crepe	100 ^k
Zinc Oxide	10
Clay	50
Whiting	125
Stearic Acid	1
Cycline Oil	4
Sulphur	3
Thiofide	1 8
Thiuram DS	0 2
RSL Colour	1 5

The cure is the same for both mixes, i.e. from 4 to 7 minutes at 287 °F

White Soles.

Rubber	100 ^k
Zinc Oxide	25

Clay	...	35 ^k
Titanium	25
Stearic Acid	0 5
Cycline Oil	3
Sulphur	2 25
Thiofide	1 2
Thiuram DS	0 1

Hot air cure: 60 minutes rise, 70 to 100 minutes
at 255 ° F. with 30 lbs. air pressure.

Bathing Caps.

Pale Crepe	100 ^k
Zinc Oxide	5
Stearic Acid	...	0 5
Sulphur	2 5
Thiofide	0 75
Thiuram DS	0 10
RSL Colour	1

Cure: 6 minutes at 312 ° F.

Tiling Stock—Flooring.

White.

Pale Crepe	100 ^k
Zinc Oxide	50
Lithopone	100
Whiting	125
Clay	150
Stearic Acid	2
Cycline Oil	4
Paraffin Wax	2
Sulphur	3
Thiofide	1 5
Thiuram DS	1 2

Blue to whiten

Cure: 10 minutes at 307 ° F.

Coloured.

Pale Crepe	100 ^k
Zinc Oxide	10 to 20
Lithopone	0 to 20
Whiting	...	175
Clay	150
Stearic Acid	2
Cycline Oil	4
Paraffin Wax	2
Sulphur	3
Thiofide	1 5
Thiuram DS	0 2
RSL Colour		to suit
Cure: 10 mins. at 307 ° F.		

It may be pointed out that these latter two stocks are quite rigid. Less hard compounds may be obtained by lowering the whiting content without altering any other ingredients.

The following two formulas indicate the practical value of *Ultra Zinc DMC added to Thiofide Stock*.

Black Shoe Upper.

Smoked Sheets	100 ^k
Zinc Oxide	25
Whiting	60
Clay	15
Carbon Black	2
Stearic Acid	1
Cycline Oil	3
Sulphur	...	2
Thiofide	1 35
Ultra Zinc DMC		0 10
Flectol B or H	1 25

Hot air cure: 60 mins. rise followed by 40 to 70 minutes at 255 ° F. with 30 lbs. air pressure.

Hot Water Bottles.

Smoked Sheets	100 ^k
Zinc Oxide	10
Whiting	80
Stearic Acid	1
Cycline Oil	2
Sulphur	2 5
Thiofide	0 60
Ultra Zinc DMC		0 10
RSL Colour	1 25

Cure: 8 to 10 minutes at 298° F.

The following *Imperial Chemical Industries* formulas are composed using their special products:-

A high class mix for **Transparent Moulded Goods with Vulcafor P.**

Pale Crepe	100 ^k
Sulphur	1 8
Zinc Oxide Active	0 5
Paraffin Oil	0 7
Stearic Acid	0 35
Vulcafor P	0 35

Cure: 10 to 15 minutes at 248° F.

Here is a recipe for obtaining **Transparent Articles** by using the I. C. I. Vulcafor DHC.

Pale Crepe	100 ^k
Zinc Oxide	1
Zinc Carbonate	1
Stearic Acid	1
Sulphur	2
Vulcafor DHC	0 375

Cure: 7 minutes at 285° F.

This accelerator should be a boon for those interested in Dry-Heat-Cured Foot Wear Articles,

especially with its anti-ageing properties. Vulcafor DHC exhibits a remarkable stability towards friction as brought about when mixes are spread or frictioned on fabric.

Another recipe for a good quality **Black Boot Upper Compound**.

Smoked Sheets	100 ^k
Zinc Oxide	40
Gas Black	6
Light Magnesium Carbonate	10
Vulcaflex A	0 7
Whiting	40
Stearic Acid	0 5
Ceresine Wax	0 5
Sulphur	2
Vulcafor DHC	2

Cure: 10 to 15 minutes at 248° F.

Besides this, the accelerator finds a wide application in the manufacture of **Gas Tubings, Bathing Caps, Flooring, Matting, Coloured Soles and Heals**.

It has also been successfully used in the manufacture of **Sponges** and a typical recipe is given below:-

Softened Pale Crepe	100 ^k
Zinc Oxide 5
Precipitated Chalk	40
Lithopone 3
Vaseline 3
Vulcazote A*	... 10
Paraffin Oil 5

* Cover the hands completely while using the product and do not allow it to come into contact with any part of the skin.

Kerosene	5 ^k
Sulphur	2
Vulcafor DHC	0 25
Vulcafor colour	As desired
Cure: 60 minutes at 258 ° F.		

CHAPTER XI.

Miscellaneous.

Temperature Scales

Centigrade—Fahrenheit

— 273.13 °C corresponding to 459.6 °F = Absolute Zero

C.	F.	C.	F.	C.	F.
-50	—58	—4	24.8	50	122
-45	—49	—3	26.6	55	131
-40	—40	—2	28.4	60	140
-35	—31	—1	30.2	65	149
-30	—22	0	32	70	158
-25	—13	+1	33.8	75	167
-20	—4	5	41	80	176
-17.8	0	10	50	85	185
-15	+5	15	59	90	194
-10	14	20	68	95	203
—9	15.8	25	77	100	212
—8	17.6	30	86	101	213.8
—7	19.4	35	95	102	215.6
—6	21.2	40	104	103	217.4
—5	23	45	113	104	219.2
				105	221

C.	F.	C.	F.	C.	F.
106	222.8	136	276.8	166	330.8
107	224.6	137	277.6	167	332.6
108	226.4	138	280.4	168	334.4
109	228.2	139	282.2	169	336.2
110	230	140	284	170	338
111	231.8	141	285.8	171	339.8
112	233.6	142	287.6	172	341.6
113	235.4	143	289.4	173	343.4
114	237.2	144	291.2	174	345.2
115	239	145	293	175	347
116	240.8	146	294.8	176	348.8
117	242.6	147	296.6	177	350.6
118	244.4	148	298.4	178	352.4
119	246.2	149	300.2	179	353.2
120	248	150	302	180	356
121	249.8	151	303.8	181	357.8
122	251.6	152	305.6	182	359.6
123	253.4	153	307.4	183	361.4
124	255.2	154	309.2	184	363.2
125	257	155	311	185	365
126	258.8	156	312.8	186	366.8
127	260.6	157	314.6	187	368.6
128	262.4	158	316.4	188	370.4
129	264.2	159	318.2	189	372.2
130	266	160	320	190	374
131	267.8	161	321.8	191	375.8
132	269.6	162	323.6	192	377.6
133	271.4	163	325.4	193	379.4
134	273.2	164	327.2	194	381.2
135	275	165	329	195	383

C.	F.	C.	F.	C.	F.
196	384.8	226	438.8	256	492.8
197	386.6	227	440.6	257	494.6
198	388.4	228	442.4	258	496.4
199	390.2	229	444.2	259	498.2
200	392	230	446	260	500
201	393.8	231	447.8		
202	395.6	232	449.6		
203	397.4	233	451.4		
204	399.2	234	453.2		
205	401	235	455		
206	402.8	236	456.8		
207	404.6	237	458.6		
208	406.4	238	460.4		
209	408.2	239	462.2		
210	410	240	464		
211	411.8	241	465.8		
212	413.6	242	467.6		
213	415.4	243	469.4		
214	417.2	244	471.2		
215	419	245	473		
216	420.8	246	474.8		
217	422.6	247	476.6		
218	424.4	248	478.4		
219	426.2	249	480.2		
220	428	250	482		
221	429.8	251	483.8		
222	431.6	252	485.6		
223	433.4	253	487.4		
224	435.2	254	489.2		
225	437	255	491		

Fractional Values	
C.	F.
0.1	0.18
0.2	0.36
0.3	0.54
0.4	0.72
0.5	0.90
0.6	1.08
0.7	1.26
0.8	1.44
0.9	1.62
1.0	1.80

Conversion

Degrees Fahrenheit in Centigrade :

$$\frac{x^{\circ}\text{F} - 32}{1.8} = y^{\circ}\text{C}.$$

Degrees Centigrade in Fahrenheit:

$$(x^{\circ}\text{C} \times 1.8) + 32 = y^{\circ}\text{F}.$$

Melting Point of Rosins

Cumaron	266° F - 130° C
Rosin	212° F - 100° C
Sandarac	280.4° F - 138° C
Shellac	248° F - 120° C

Melting Point of Waxes

Beeswax	145.4° F - 63° C
Carnauba	183.2° F - 84° C
Ceresine	167° F - 75° C
Montan	176° F - 80° C
Ozokerite	158° F - 70° C
Paraffin	131° F - 55° C

Specific Gravity and Specific Volume.

1. Specific Gravity is the ratio between the weight of unit volume of a substance and the weight of the same volume of water at a given temperature—usually at 60° F. (15.5° C.) or 20° C., or 4° C.—Specific gravity multiplied by 1000 gives the weight of 1 cubic foot in ounces avoirdupois, or the weight of 1 liter (cubic decimeter) in grams.

2. Specific volume, which is the reciprocal of specific gravity (1 divided by specific gravity), represents the volume in liters of 1 kg., or the volume in cubic feet of 1000 ounces. It also represents the ratio between the volume of 1 lb. of water (27.72 cu. in.) and the volume of 1 lb. of the material in question.

To Figure the Specific Gravity of a Compound.

1. Express the weight of each ingredient in kilograms, or in pounds and decimal fractions thereof, but not in pounds and ounces.

2. Divide the weight of each ingredient by its specific gravity (or multiply the weight by the specific volume), add the results together and divide the sum into the total weight of the compound.

Example.

Weight Kg. or lb.		Sp. Gr.		Volume Liters or lb. Vol.	
Rubber 100	0.92	=	108.70	
Stearic acid 3	0.92	=	3.26	
Zinc Oxide 80	5.65	=	14.20	
Sulphur 3	2.05	=	1.46	
Accelerator 1	1.42	=	3.70	
Total	187			128.32	
Specific Gravity	$\frac{187}{128.32}$		=	1.457	
Specific Gravity found for the cured stock		=	1.455	

The Specific gravity of Hevea Rubber runs from 0.91 to 0.92 for the best grades, i.e., Fine Para. Pale Crepe, Smoked Sheets. In the majority of cases, with modern low sulphur compounds, the best agreement between the *calculated and determined specific gravity is obtained* when the value 0.91 or 0.92 is used for rubber.

Specific Gravity of Rubber Materials

	Sp. Gr.	Sp. Vol
Antimony, Crimson (Sulphur Free)	3.60	.278
Antimony, Golden (Pure: 15-17% Free Sulphur)	3.20	.313
Antimony, Golden (55% Calcium Sulphate: 15-17% Free Sulphur).	2.54	.394
Asbestine	2.85	.351
Asphalt, Liquid	1.00	1.000
Balata	.97	1.031
Barium Carbonate	4.33	.231
Barytes, White	4.45	.225
Beeswax	.96	1.042
Bentonite	2.41	.415
Blanc Fixe	4.20	.238
Cadmium Sulphite, Yellow	4.58	.218
Carbon Black, Channel	1.80	.555
Carnauba Wax	.99	1.010
Casein	1.26	.793
Ceresin, White	.93	1.075
Chromium Oxide, Green	4.95	.202
Clay Dixie	2.60	.385
Coal Tar Pitch	1.25	.800
Glue	1.27	.787
Graphite, Flake	2.36	.426
Gutta Percha,	.98	1.020
Infusorial Earth (Fossil Flour)	2.15	.465
Iron Oxide, Red (98%)	5.14	.195
Iron Oxide, Red (Spanish)	4.56	.219
Kalite	2.66	.376
Lamp Black	1.78	.562
Lead Sublimed Blue	6.67	.150
Lime Hydrated	2.08	.481
Litharge	9.35	.107

	Sp. Gr.	Sp. Vol.
Lithopone (30% Zinc Sulphite)	4.20	.238
Magnesium Carbonate Light	2.23	.448
Magnesium Oxide, Heavy	3.20	.313
Mica, Powdered	2.95	.339
Mineral Rubber (Hard Hydrocarbon) ..	1.04	.961
Montan Wax95	1.087
Ocher	2.80	.357
Oil, Cottonseed92	1.087
Oil, Palm92	1.087
Oil, Pine Tar99	1.010
Oil, Rosin98	1.020
Oleic Acid90	1.111
Ozokerite Green93	1.075
Paraffin Wax91	1.099
Petrolatum, White88	1.136
Petrolatum, Amber88	1.136
Petrolatum, Green88	1.136
Pine Tar	1.10	.909
Prussian Blue	1.85	.541
Rosin	1.07	.935
Rubber Hevea92	1.087
Silica	2.65	.377
Slate, Powdered	2.80	.357
Soapstone, Powdered	2.85	.351
Sodium Bicarbonate	2.20	.455
Stearic Acid92	1.087
Substitute, (Factice) Para	1.04	.961
Substitute, (Factice) Brown	1.04	.961
Substitute, (Factice) White	1.04	.961
Sulphur	2.05	.488
Talc	2.84	.352
Therminatomic Carbon P-33	1.80	.555
Thermax	1.80	.555
Thiocarbanilide	1.28	.781
Titanium Dioxide (Pure)	3.94	.254

	Sp. Gr.	Sp. Vol
Titanium Dioxide (Barium Base)	4.30	.233
Titanium Dioxide (Calcium Base)	3.13	.319
Triphenylguanidine	1.10	.909
Ultramarine Blue	2.35	.426
Vermillion, English	8.10	.124
Whiting, Natural	2.71	.369
Whiting, Precipitated	2.71	.369
Whiting, Gilders	2.71	.369
Zinc Carbonate	3.86	.259
Zinc Oxide	5.65	.177
Zinc Stearate	1.05	.952
Zinc Sulphite	4.00	.250

Mensuration Formulas.

Circumference of a circle = diameter x 3.1416.

Radius of a circle = circumference x .159155.

Diameter of a circle = circumference x .31831.

Side of an inscribed equilateral triangle = diameter of circle x .86.

Side of an inscribed cube = radius of sphere x 1.1547.

Side of an inscribed square = diameter of circle x .7071
= circumference of circle x .225.

Area of a circle = radius² x 3.1416
= diameter² x .7854
= circumference² x .07958.

Area of a square = a side².

Area of a triangle = base x $\frac{1}{2}$ altitude.

Area of a rectangle = base x altitude.

Area of a parallelogram = base x altitude.

Area of a trapezoid = altitude x $\frac{1}{2}$ sum of parallel sides.

Area of a parabola = $\frac{2}{3}$ base x altitude of exterior triangle.

Area of a trapezium = area of the two constituent triangles.

Area of a regular polygon = $\frac{1}{2}$ the perpendicular from the centre to one of the sides x sum of the sides.

Area of a sector = $\frac{1}{2}$ radius x arc.

Area of an ellipse = $\frac{1}{2}$ short diameter x $\frac{1}{2}$ long diameter x 3.1416.

Surface of a sphere = circumference x diameter
= diameter² x 3.1416.

Surface of a cube = area of one side x 6.

Surface of a cylinder = area of both ends + (length x circumference).

Surface of a zone or convex surface of segment of a sphere = 6.2832 x radius of sphere from which it is cut x altitude of the zone.

Surface of a frustum of a cone = $\frac{1}{2}$ (sum of circumferences at both ends) x slant height + area of both ends.

Volume of a sphere = surface x $\frac{1}{6}$ diameter
= diameter³ x .5236.

Volume of a cube = one side³.

Volume of a cylinder or prism = area of end x length.

Volume of a cone or pyramid = area of base x $\frac{1}{3}$ altitude.

Volume of a frustum of a cone or pyramid = $\frac{1}{3}$ altitude x area of both ends + square root of area of both ends multiplied together.

Volume of a wedge = area of base x $\frac{1}{2}$ altitude.

Volume of a spherical segment of one base = $\frac{1}{2}$ altitude x 3.1416 x radius of base² + $\frac{1}{6}$ altitude³ x 3.1416.

Useful Factors and Constants.

1 horse power = 0.746 kilowatt.

1 boiler horse power = the work of converting 30 lbs. of water per hour from an initial temp. of 100° F. to

steam at 70 lbs. gauge pressure; or the evaporation of $34\frac{1}{2}$ lbs. of water per hour at 212° F. into steam at 212° F.

1 watt = 0.0134 horse power = 44.3 foot pounds per min.

1 kilowatt = 1000 watts = 1.341 horse power = 44300 foot pounds per min.

1 gram weight = 981 dynes (force) approximately.

1 British thermal unit (BTU) = 252 calories (gram).

1 gram calorie = 4.185 joules.

? Heat of fusion of water = 179.24 calories per gram.

Heat of vaporisation of water = 535.9 calories per gram.

1 atmosphère = 14.7 lbs. per sq. in. = 1.0333 kilograms per sq. cm.

1 kilogram per sq. cm. = 0.9677 atmosphere = 14.22 lbs. per sq. in.

1 inch (pressure) of mercury = 13.6 inches of water.

Coefficient of expansion of gases = .003665 per degree C.

Density of dry air at 0° C. and 760 mm. = .001293 grams per cc.

Density of sea water = 1.025 grams per cc.

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PRINTED AND PUBLISHED BY THE AUTHOR
AT THE SANTA CRUZ PRESS, ALLEPPEY, TRAVANCORE.